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Polynuclear Aromatic Compounds
Synthesis and Purification

Oklahoma State Univ.
Stillwater

Prepared for

Environmental Sciences Research Lab.
Research Triangle Park, NC

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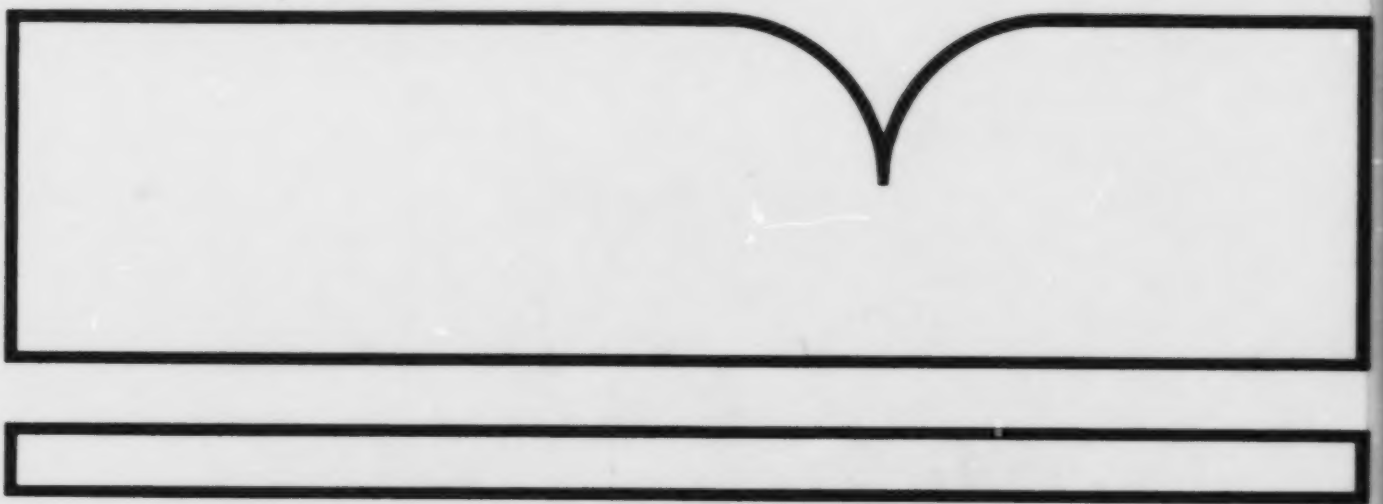

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POLYNUCLEAR AROMATIC COMPOUNDS
Synthesis and Purification

by

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Grant No. 805419

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ABSTRACT

Synthesis and/or purification of a group of polynuclear aromatic (PNA) compounds commonly found as pollutants in the environment are reviewed and discussed. Details of the experimental procedures and techniques as well as chromatographic and spectroscopic evidence of structure and purity of the compounds supplied to the U.S. Environmental Protection Agency are presented. In addition, the apparatus designed and constructed to meet the synthesis needs together with safety improvements for handling toxic compounds are described. Publications resulting from this work and manuscripts in preparation are cited.

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Other mass and NMR determinations were obtained from Oklahoma State University Chemistry Department instruments. The use of the Varian XL-100 NMR spectrometer obtained from NSF Grant CHE76-05571 is gratefully acknowledged.

SECTION I

This report describes the work involved in the continuation of our earlier EPA grant 803097 (EPA-600/2-78-006) and the objective of providing 10-gram samples of highly purified polynuclear aromatic compounds for use as instrumental standards by the Chemistry and Physics Laboratory, National Environmental Research Center, Research Triangle Park, North Carolina 27711 was continued in the current effort. The list of the needed compounds, sorted into hydrocarbons, nitrogen heterocyclics and oxygen heterocyclics, is shown in Table 1.

Table 1. AROMATIC COMPOUNDS CONSIDERED FOR SYNTHESIS AND PURIFICATION

Hydrocarbons	Nitrogen Heterocyclics
Benzo[*ghi*]fluoranthene[a]	Acridine[b]
11H-Benzo[*b*]fluorene[a]	Benz[*a*]acridine[a]
Benzo[*e*]pyrene[b]	Benz[*c*]acridine[a]
Cholanthrene[c]	Benzo[*lmn*]phenanthridine[d]
Coronene[b]	Benzo[*f*]quinoline[b]
Cyclopenta[*c,d*]pyrene[d]	Benzo[*h*]quinoline[b]
Dibenz[*a,h*]anthracene[a]	Dibenz[*a,h*]acridine[a]
Dibenzo[*a,i*]pyrene[c]	Dibenz[*a,j*]acridine[a]
Dibenzo[*a,l*]pyrene[a]	Indeno[1,2,3-*i*]isoquinoline[c]
Dibenzo[*c,g*]phenanthrene[d]	11H-Indeno[1,2-*b*]quinoline[b]
5,6-Dihydro-4H-dibenz[*a,kl*]anthracene[d]	Phenanthridine[b]

(continued)

TABLE 1 (continued)

Hydrocarbons (continued)	Nitrogen Heterocyclics (continued)
Indeno[1,2,3-*cd*]pyrene[c]	2-Phenyldibenz[*c*,*h*]acridine[a]
3-Methylcholanthrene[a]	Oxygen Heterocylics
Naphtho[2,3-*e*]pyrene[a]	Benz[*a*]anthracene-7,12-dione[d]
1,2,7,8-Tetrahydrodibenzo[*c*,*g*]phenanthrene[d]	7H-Dibenz[*a*,*kl*]anthracene-7-one[a]
	Dinaphtho-[2,1-*b*:1',2'-*d*]furan[b]
	Peri-Xanthene-xanthene[b]

[a]Synthesis not attempted. [b]Completed and shipped. [c]Synthesis attempted but not completed. [d]Synthesis remaining under study.

During the past three years we have synthesized and/or purified 18 compounds for the EPA. Eight of these compounds may be found listed in Table 1. The remaining 10 are shown in Table 2. The latter group resulted in part from other syntheses carried out by our group principally for the Thermodynamics group of the U.S. Department of Energy, Bartlesville Energy Research Center. In this connection equipment and supplies were shared to reduce costs. In summary, our synthesis effort resulted in the preparation and/or purification of 10 hydrocarbons, 6 nitrogen heterocyclic compounds, and 2 oxygen heterocyclic compounds.

SECTION 2

CONCLUSIONS

The synthesis and chemistry of PNA compounds still remain of interest to a broad spectrum of industrial and governmental laboratories. These compounds are an integral part of petroleum, petroleum products, coal liquids, and shale oil. While there is a diminished current interest in pure aromatic compounds in air pollution studies, other environmental problems requiring high purity standards involving PNA compounds are bound to emerge as the use of coal, coal liquids, heavy petroleum fractions, and shale oil which are rich in polynuclear aromatics and their hydrogenated derivatives are handled and used.

SECTION 3

RECOMMENDATIONS

As pointed out in the preceeding section, the current hiatus in synthesis of PNA compounds will eventually pass since there will be increased need for definitive studies in several areas as environmental problems increase. Future efforts will probably shift to partially reduced aromatic compounds including heterocyclics since these are major constituents of coal liquids and shale oil.

In our earlier report (EPA-600/2-78-006), we suggested that the use of stable isotopes as labels in PNA aromatics and their partially hydrogenated derivatives will become more important and systematic synthesis of representative labelled compounds should be initiated. The pure standard samples (labelled and unlabelled) should be available to meet the requirements posed by advances in instrumentation and the pressure of new events and pollution problems.

SECTION 4

MATERIALS AND METHODS

The synthesis effort described in this report includes hydrocarbon and nitrogen heterocyclic compounds as well as oxygen heterocyclic compounds. Those supplied to the EPA during the reporting period are listed in Table 2 and these are grouped alphabetically within the respective categories. The structures are presented as they appear in the discussion of synthesis and purification. The page number of the first appearance of the structure and the sample size supplied to the EPA are also given in Table 2. These samples generally were contained in about 100 vials and ranged from 9.9 to 13.7 g.

TABLE 2. COMPOUNDS SUPPLIED TO THE EPA DURING THE REPORTING PERIOD

Hydrocarbons

Benzo[*ghi*]perylene(1)[a], mp 276-277°C, 10.4 g, p. 9

Benzo[*e*]pyrene(2)[a], mp 178-179°C, 9.96 g, p. 10

Chrysene(3)[a], mp 251-253°C, 11.6 g, p. 7

Coronene(4)[a], mp 437-440°C, 10.5 g, p. 4

1,2,3,6,7,8-Hexahydropyrene(5)[b], mp 133-134°C, 10.0 g, p. 10

sym-Octahydroanthracene(6)[b], mp 72-73°C, 13.7 g, p. 7

Perylene(7)[a], mp 275-277°C, 13.2 g, p. 9

1,2,3,4-Tetrahydroanthracene(8)[b], mp 89-90°C, 10.3 g, p. 12

4,5,9,10-Tetrahydropyrene(9)[b], mp 139-140°C, 10.4 g, p. 11

1,10-Trimethylenephenanthrene(10)[a], mp 80.5-81.0°C, 13.2 g, p. 12

TABLE 2 (continued)

TABLE 2 (continued)

Nitrogen Heterocyclics

Acridine(11)[a], mp 109-110°C, 12.7 g, p. 7

Benzo[*f*]quinoline(12)[a], mp 90-91°C, 12.9 g, p. 7

Benzo[*h*]quinoline(13)[a], mp 50.5-51.5°C, 11.1 g, p. 7

Carbazole(14)[a], mp 243-244°C, 10.5 g, p. 7

11H-Indeno[1,2-*b*]-quinoline(15)[a], mp 167-169°C, 10.7 g, p. 13

Phenanthridine(16)[a], mp 106.5-107.5°C, 12.1 g, p. 7

Oxygen Heterocyclics

Dinaphtho[2,1-*b*: 1',2'-d]furan(17)[a], mp 156-157°C, 10.7 g, p. 13

peri-Xanthenoxanthene(18)[a], mp 241-242°C, 9.7 g, p. 13

[a]Listed in Table 1 or the original list of EPA-600/2-78-006.

[b]Compound resulted from shared effort.

COMPOUNDS OBTAINED THROUGH PURIFICATION OF AVAILABLE MATERIALS

Purification Techniques

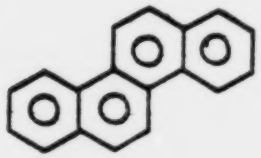
Purification is a significant step in providing pure compounds. In the earlier report (EPA-600/2-78-006) we described some techniques and apparatus. These are currently used and have become an important addition to our laboratory practice.

Because the synthesis products and intermediates frequently are carcinogenic, we reviewed our procedures and offer this experience in Appendix A. This includes the use of an improved Soxhlet apparatus,[1] a modified sublimation apparatus,[2] solid sample dispenser,[3] and an apparatus to clean laboratory items.[4] We have also used zone refining for purification. To improve this method, we redesigned our zone refining apparatus and include a description of this in Appendix B.

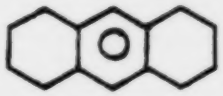
Seven of the supplied compounds were either available from other work[5] or commercially available and hence synthesis was not required.

Hydrocarbons Obtained Through Purification

Commercial chrysene (3) required purification as described under Experimental. It was completed during the transition from EPA grant 803097 and its ^{1}H NMR spectrum was included in EPA-600/2-78-006 report. Sym-Octahydroanthracene (6) was purified through preparative high-pressure liquid chromatography[6] (HPLC) and served as a model compound for this new separation method. This is described in EXPERIMENTAL PROCEDURES.

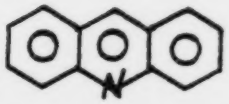


Chrysene (3)

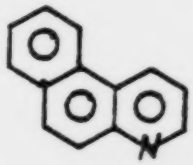


sym-Octahydroanthracene(6)

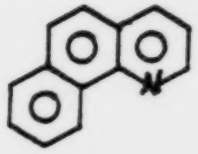
Nitrogen Heterocyclics Obtained Through Purification



Acridine (11)

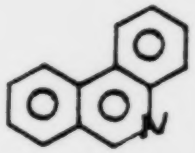


Benzo[f]quinoline (12)



Benzo[h]quinoline (13)

Carbazole (14)



Phenanthridine (16)

Samples of the above nitrogen heterocyclic aromatic compounds were obtained through purification of commercially available material. These purifications were uneventful except that acridine (11) resisted the usual purification procedures and required complexation with catechol.[7] Carbazole (14) could not be zone refined because of persistent tube rupture during the zone-refining process.[8] It was purified by repeated elution through alumina with n-hexane.[1]

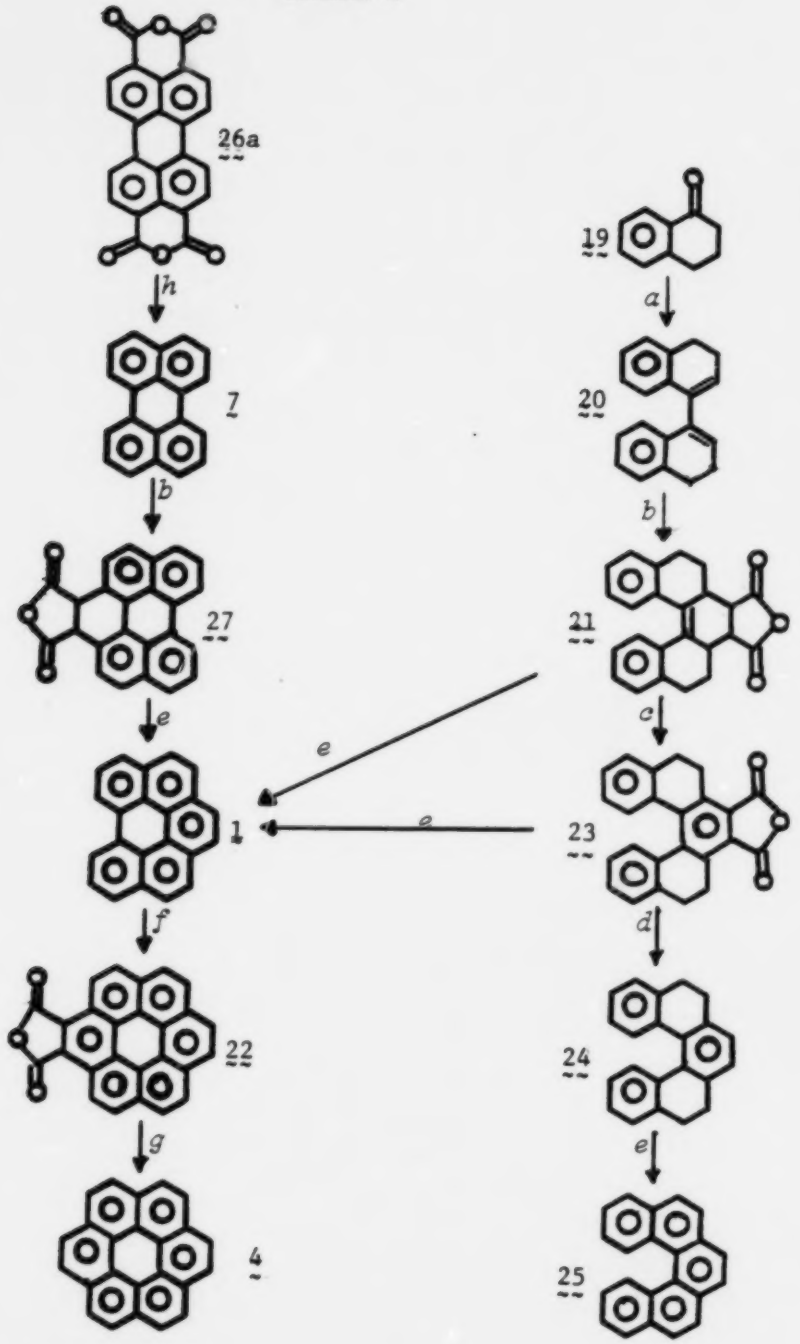
COMPOUNDS SYNTHESIZED

Benzo[*ghi*]perylene (1), Coronene (4), Perylene (7)

The synthesis of 1, 4, and 7 is shown in Scheme 1. We originally hoped to prepare coronene 4 from perylene (7). However, commercial perylene is expensive and difficult to purify and the synthesis of 1 or 4 via 7, though short, is less convenient than synthesis via 19 which provides a cleaner product. Hydrocarbons 24 and 25 of Scheme 1 remain a possibility.

Because of the high melting point of coronene and because of the increased scale of reaction in its synthesis, we found it advantageous to develop the glassware and the sand-bath heater shown in Appendix C. This heater readily develops and maintains a reaction temperature of 500°C. The independent control of temperature at the three zones is a distinct advantage. Use of the glass vessel of Appendix C and the heater enabled a 6-fold increase in reaction scale for step g of Scheme I. This apparatus was also used in the purification of 22 through vacuum sublimation and permitted a 66-fold increase in purification scale over what had previously been reported.[9] Without the apparatus our synthesis of 1 and 4 would have been impractical since an excessive repetition of runs would have been required.

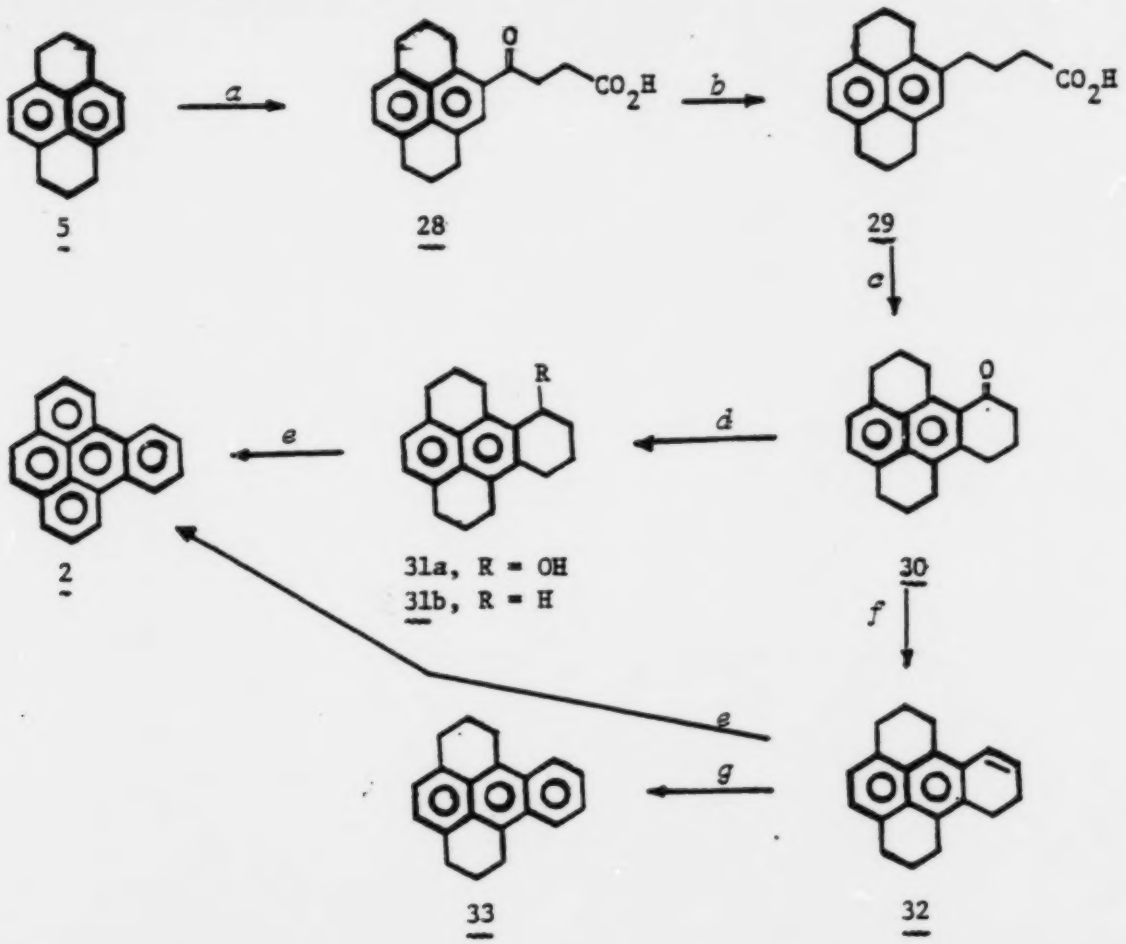
SCHEME 1



[a] Al, C_6H_6, C_2H_5OH, $HgCl_2$; HOAc, Ac_2O. [b] Maleic anhydride, Δ. [c] Br_2, $CHCL_3$. [d] Cu_2O in refluxing quinoline. [e] Pd/C, Δ. [f] Maleic anhydride, chloranil, Δ. [g] Soda lime, Δ. [h] Soda lime, Zn dust, Δ.

Benzo[*e*]pyrene (2), 1,2,3,6,7,8-Hexahydropyrene (5), 4,5,9,10-Tetrahydropyrene (9)

Pyrene (EPA-600/2-78-006) was reduced with Na in a variety of alcohols to provide 5 for use as starting material in the synthesis of 2 as shown in Scheme 2. Figure 1 clearly shows why Na and alcohol reduction of pyrene is superior to catalytic hydrogenation in the preparation of 5, conversely for the synthesis of dihydro- and tetrahydropyrene, catalytic hydrogenation of pyrene was found to be the better route.



[a]Succinic anhydride, $AlCl_3$, $C_2H_5NO_2$. [b]Pd/C, H_2, CH_3CO_2H, Δ. [c]PPA, Δ. [d]$NaBH_4$. [e]Pd/C, Δ. [f]$(ibu)_2AlH$; H^+, $-H_2O$. [g]Pd/C, toluene, Δ.

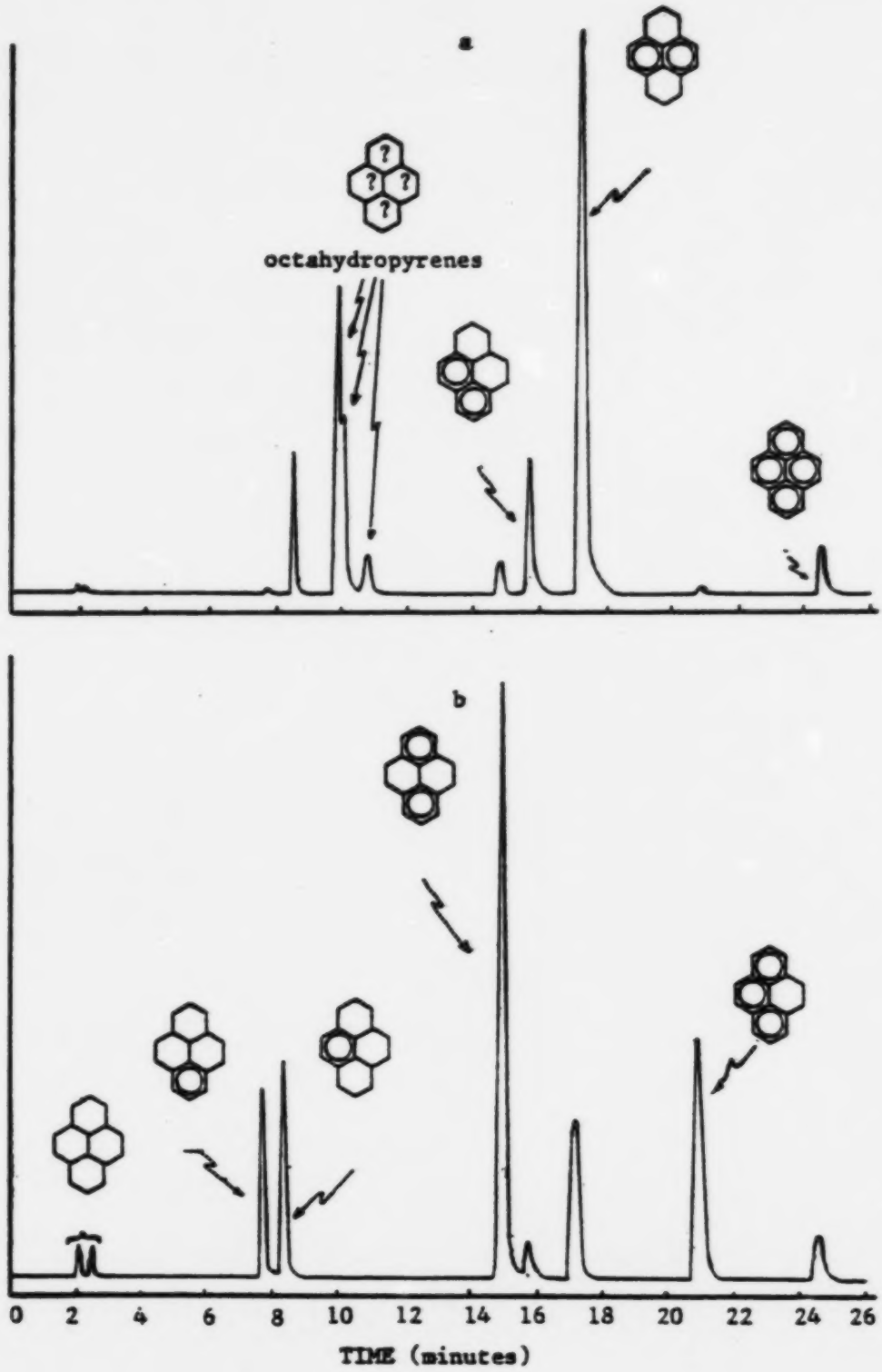
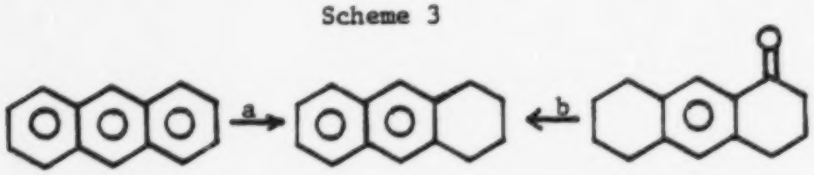


Figure 1. G.C. Retention Pattern Obtained from a) Dissolving Metal Reduction of Pyrene and b) Catalytic Hydrogenation of Pyrene.

1,2,3,4-Tetrahydroanthracene (8)

Anthracene (34) served as a model in developing hydrogenation techniques. With Rh/C we were able to selectively prepare 8.[10] This hydrocarbon has recently been obtained from the tetrahydroanthracenone (35) by heating it in the presence of NaOH·KOH as shown in Scheme 3.[11]

Scheme 3



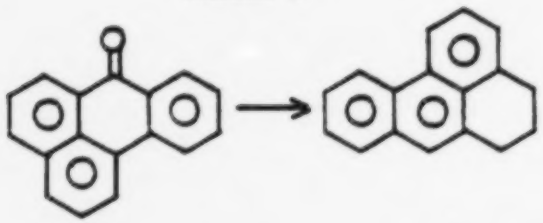
34 8 35

[a] H_2, Rh/C. [b] KOH· NaOH, Δ.

1,10-Trimethylenephenanthrene (10)

Hydrocarbon 10 was prepared by reduction of benzanthrone[12] as shown in Scheme 4.

Scheme 4



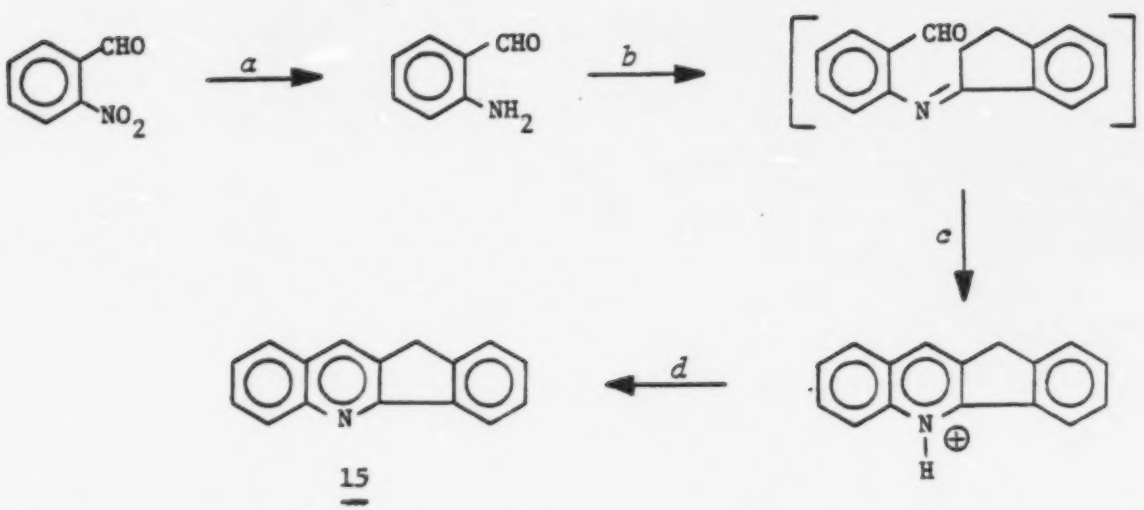
36 10

[a] HI, P_4, Δ.

11H-Indeno[1,2-*b*]quinoline (15)

Amine 15 was readily prepared as shown in Scheme 5.[13]

Scheme 5



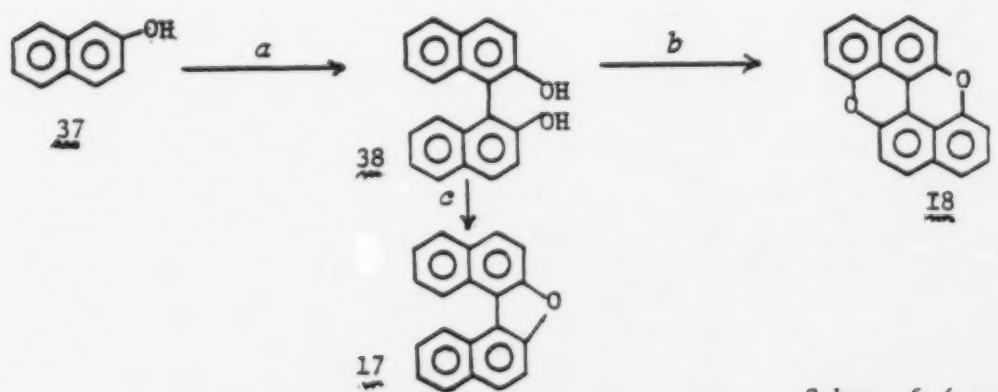
15

$^{a}Fe^{++}$, NH_4OH, steam. ^{b}1-Indanone. ^{c}HCl. ^{d}NaOH.

Dinaphtho[2,1-b:1',2'-d]furan (17) and peri-Xanthenoxanthene (18).

Compounds 17 and 18 were synthesized as shown in Scheme 6. In the early efforts to prepare perylene (7), we tried using the diphenol 38 as starting material, since a high yield conversion of 37 to 7 had been reported.[14] However, we were unable to duplicate the reported yields and concluded that a mixture of 7 and 17 with some 18 probably resulted. Accordingly, 17 and 18 were prepared as shown in Scheme 6.[15]

Scheme 6



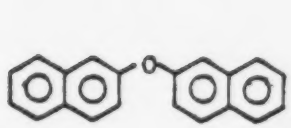
37 38 17 18

Scheme 6 (continued)

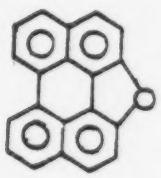
Scheme 6 (continued)

[a] $FeCl_3$, H_2O. [b] CuO, $C_6H_5NO_2$. [c] V_2O_5, Δ.

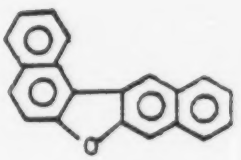
High pressure liquid chromatography studies using 18, 38, 39a, 39b, 40, 1,1'-binaphthyl showed that 17 was free of these likely impurities. Compound 17 has been reported to be light yellow in appearance, but the



39a



39b



40

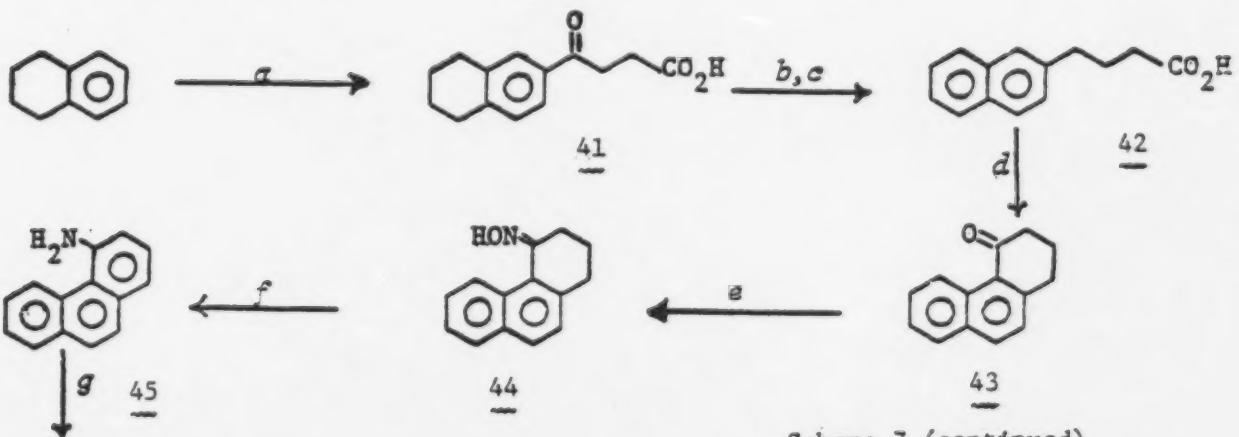
purified 17 is colorless. Compound 17 was first obtained as a 50-80% yield side product in the conversion of β-naphthol to perylene in the presence of phosphorous acid and phorphorous pentachloride.[14]

CURRENT SYNTHESIS

Benzo[*lmn*]phenanthridine (47).

We have carried the synthesis of benzo[*lmn*]phenanthridine (4-azopyrene) (47) to the preparation of oxime 44. We believe the remaining steps of Scheme 7 to be viable.[15] We hope to finish this synthesis.

Scheme 7



Scheme 7 (continued)

Scheme 7 (Continued)

46 47

[a]Succinic anhydride, $AlCl_3$, $C_2H_5NO_2$. [b]H_2, Pd/C, CH_3CO_2H, Δ. [c]Pd/C, Δ. [d]PPA, Δ. [e]$NH_2OH \cdot HCl$. [f]Ac_2O; HCl, Δ. [g]HCO_2H.

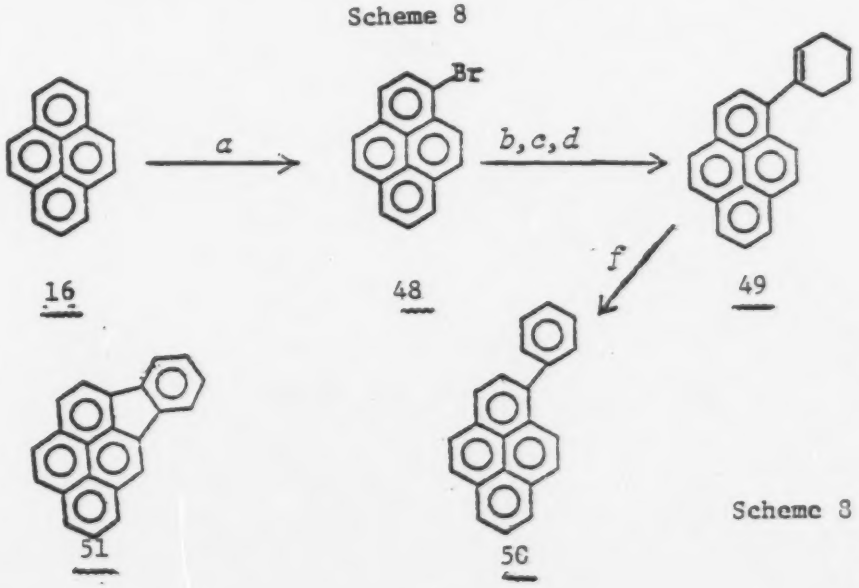
At the termination of the project, other syntheses remained incomplete. This resulted because some reactions failed or the yield was too low for a practical synthesis. The compounds involved are indeno[1,2,3-cd]pyrene (51), cholanthrene (55), and indeno[1,2,3-*i*]isoquinoline (62) shown in Schemes 8, 9, and 10 respectively.

INCOMPLETE SYNTHESES

Indeno[1,2,3-cd]pyrene (51)

Hydrocarbon 51 was prepared in sufficient quantity to obtain a sample for instrumental studies. However the yield and purity of the product was inadequate to provide a sample.[16]

Scheme 8



16 48 49

51 50

Scheme 8 (continued)

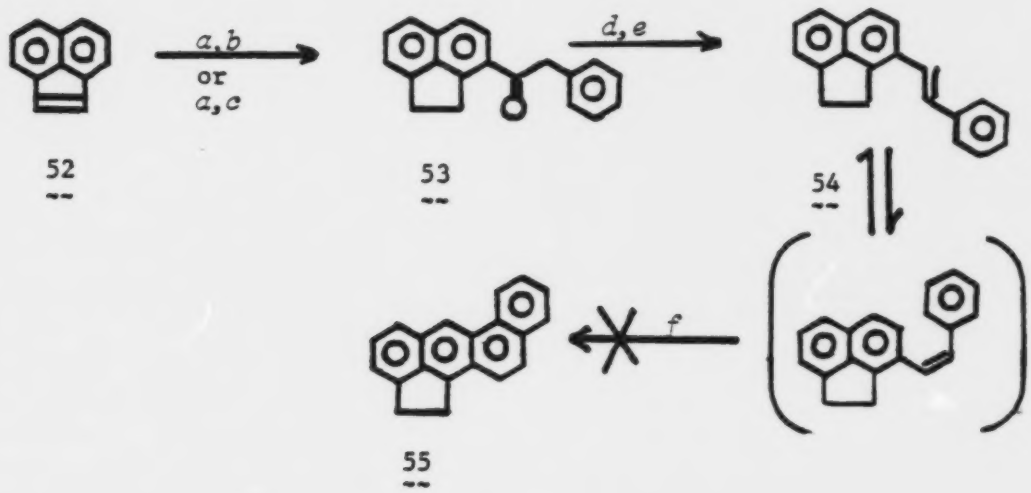
Scheme 8 (continued)

[a] $CuBr_2$, CCl_4. [b] n-BuLi, Et_2O. [c] Cyclohexanone. [d] Acidic alumina. [e] Pd/C, Δ. [f] $AlCl_3$, NaCl melt.

Cholanthrene (55)

We attempted the synthesis of 55 using the route in Scheme 9 and readily prepared 54.[17] However, the last step (photocyclization) failed. At this time, we do not know whether this reaction failed because of lack of

Scheme 9



52 53 54 55

[a] B_2H_6, THF. [b] Acetic Acid. [c] Phenylacetic acid. [d] $(iBu)_2AlH_4$. [e] p-TSA, Δ; $-H_2O$. [f] hν, I_3.

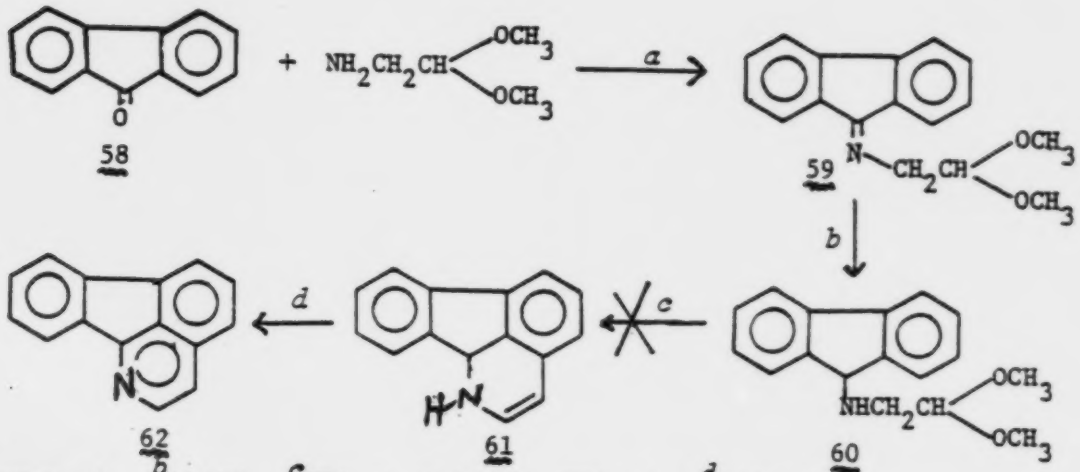
isomerization of cis to trans or in the cyclization step. A similar reaction sequence[18] was successfully used to convert 56 to 57.

56 57

Indeno[1,2,3-*i*]isoquinoline (62)

We sought 62 as shown in Scheme 10.[19] Compound 60 was prepared but cyclization failed to take place.

Scheme 10



[a]Toluene, Δ. [b]$LiAlH_4$. [c]PPA, Δ or H_2SO_4, PPA, Δ. [d]Pd/C, Δ.

SECTION 5

EXPERIMENTAL PROCEDURES

The synthesis routes used in our work are presented in SECTION 4 and some experimental details have been prepared for publication. A list of earlier publications is presented in EPA-600/2-78-006. Other work sponsored by the EPA has been published and these papers are listed along with manuscripts under preparation on p. 64.

The experimental details will be reported in the order shown for Schemes in SECTION 4 and the respective captions.

COMPOUNDS OBTAINED THROUGH PURIFICATION OF AVAILABLE MATERIALS

Purification Techniques

This topic is treated in Appendix A.

HYDROCARBONS OBTAINED THROUGH PURIFICATION

Chrysene (3) and sym-octahydroanthracene (6)

Chrysene (3) was supplied during the interim of Grant 803097 and the current grant (805419). The ^{1}H NMR spectrum of 3 and the details of its purification were reported in EPA-600/2-78-006.

A sample of sym-octahydroanthracene (6) was prepared. This hydrocarbon served as a model for preparative high-pressure liquid chromatography[6] (HPLC) purification.

Pretreatment involved adding 6 to a Soxhlet apparatus containing a layer of acidic alumina and a layer of basic alumina (E. Merck activity). n-Hexane was used to extract 6 through the alumina layers. This extract was then passed through a column of activated silica gel.

The n-hexane solution of 6 was next injected, in 50 mL increments containing 12 g of hydrocarbon, into a Waters Prep LC-500 instrument equipped with two cartridges (5 cm x 30 cm) of silica in series.[6] n-Hexane was

used as eluant at 100 mL min. As the chromatogram developed, the front and tail portions of the peak were shaved and collected separately. The instrument was then placed on recycle and as shown in Figure 2, front and rear protions of the main peak were shaved before the peak was finally collected.

Each collected fraction was recrystallized from anhydrous methanol and then checked for purity on a Microproasil[6] column (two 4 mm x 30 cm columns in series) using n-hexane as eluant. Fractions of similar purity were combined. Those fractions which showed impurities were either reprocessed or rejected.

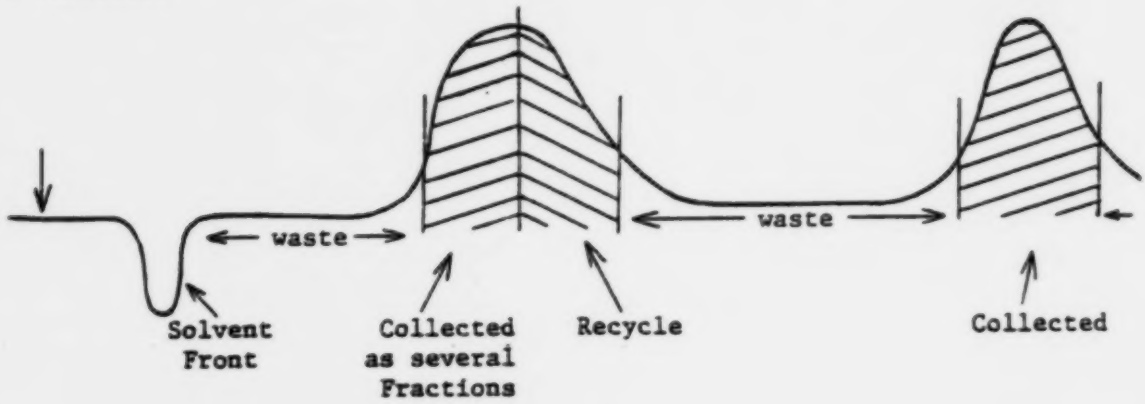


Figure 2. High Pressure Liquid Chromatographic Purification of sym-Octahydroanthracene on a Preparative Scale.

A 20.7 g sample of purified material was recrystallized from anhydrous methanol to yield 18.1 g as a first crop. This material was distilled at 90°C (0.03 mm) from silanized glassware. A 13.7 g sample, mp 72-73°, was transferred to vials under an argon atmosphere. The ^{1}H NMR spectrum appears in Figure 5.

NITROGEN HETEROCYCLICS OBTAINED THROUGH PURIFICATION

This group includes acridine 11, benzo[*f*]quinoline (12), benzo[*h*]quinoline (13), carbazole (14), and phenanthridine (16). The ^{1}H NMR spectra

may be found as Fig. 10a,11a,12a,13, and 15a. ^{13}C NMR spectra for 11, 12, 13, and 16 are shown as Fig. 10b,11b,12b and 15b.

The general purification procedure consisted of recrystallization and Soxhlet[1] treatment using basic alumina until liquid chromatography studies showed that purification had been achieved. However acridine did not respond to crystallization from several solvents and complexation with catechol was used.[7]

Acridine (11)

Acridine, previously recrystallized, was partially purified by chromatography[1] on basic alumina (Merck activity 1) using refluxing n-hexane as the eluant. The acridine crystals from the chromatography procedure were then recrystallized from ethyl acetate as yellow crystals, mp 108-109°.

Catechol complex formation was next carried out by combining acridine and catechol (1:1.1) in hot 95% ethanol (1 mol/800 mL).[7] The complex crystallized on cooling. Recrystallization from ethanol gave 83% recovery of the complex, mp 143-144°. The complex was dissociated with ether and ammonium hydroxide to give 77% recovered acridine. This material was freed of catechol by chromatography on basic alumina.[1] Sublimation at 105° (0.1 mm) gave pale yellow crystals, mp 110-111°. Analysis (LC, Microbondapak C-18) with $CH_3CN:H_2O$ indicated a purity exceeding 99.9%. The sample was placed in vials using an argon atmosphere.

Benzo[*f*]quinoline (12)

A 50 g sample of 12, previously brought to 99% purity, was placed on a 32 x5 cm column of anhydrous basic alumina (E. Merck 1076) contained in a Soxhlet column.[1] Compound 12 was then eluted with 500 mL of refluxing n-hexane contained in a 1L flask. The Soxhlet extractor was disconnected

from the cooled flask and after chilling the crystals were removed by filtration. The process was repeated twice more.

The crystals were then distilled (Kugelrohr apparatus). The product, mp 90-91°, showed an analysis of 99.98% as determined by high-pressure liquid chromatography using a C-18 Microbondapak column. An acetonitrile: water (1:1) system was used. The NMR spectra (^{13}C and ^{1}H) were consistent with the structure and showed no extraneous peaks.

Benzo[*h*]quinoline (13)

Commercial 13 was placed on top of a 5 cm layer of basic alumina contained in a 32 cm OD modified Soxhlet column.[1] Elution was complete in 1.5 hours using n-hexane as solvent. The pot volume was adjusted to 500 mL and the resulting solution was allowed to cool to room temperature and then in a refrigerator (-20°C). The crystals of 13 were collected, chromatographed, and crystallized from n-hexane two additional times following the initial procedure. After completion of the third Soxhlet extraction procedure and crystallization, the crystals were collected and distilled at 130° (0.01 mm) using a Kugelrohr apparatus.

The entire procedure was repeated two additional times to yield 13, mp 50.5-51.5°. Analytical HPLC using a C-18 column (acetonitrile:water, 1:1 and 2:1) showed 99.97% purity.

Carbazole (14)

We attempted zone refining 14 but persistent tube rupture prevented this approach. Purification was accomplished by Soxhlet extraction[1] through basic alumina (Merck activity I) with isooctane-benzene followed by recrystallization from toluene. The LC analysis showed 99.9%.

Phenanthridine (16)

Purification of 16 was achieved in the manner used for 12 and 13.

COMPOUNDS SYNTHESIZED

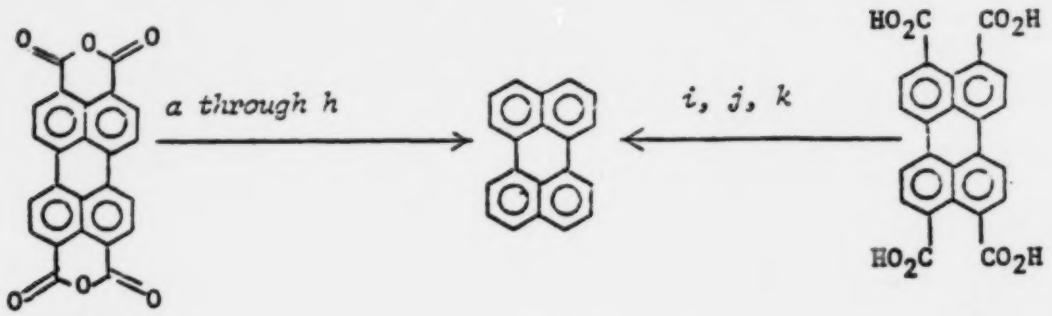
Benzo[*ghi*]perylene (1), Coronene (4), and Perylene (7) (Scheme 1)

The Conversion of 3,4,9,10-Pyrenetetracarboxylic Acid Dianhydride 26a to Perylene (7):

A 500 mL, round-bottomed flask containing 8.6 g (0.02 mol) of 26a, 63 g of finely gound soda lime and 107 g of 30 mesh Zn was evacuated to 5-10 mmHg and then immersed in a sand bath.[20] The sand bath was maintained at 440°C for 10 hr, whereupon the flask was removed and then heated briefly with an open flame. Subsequently, the entire cooled reaction mixture was transferred to a Soxhlet apparatus[1] packed with a column of 80 mL of basic alumina. Elution with toluene gave 3.2 g of 7 mp 275-276°C, as yellow-orange crystals and a second crop (0.3 g, 272-273°C). The total yield of 7 was 64%. Ten runs yielded 27.5 g of 7. The combined fractions were eluted with hot toluene from a Soxhlet extractor[1] charged with single layers of basic, neutral, and acidic alumina (60:12:35 mL, respectively) in the cited order from top to bottom. The eluate yielded 23 g of 7 which was further purified through recrystallization from acetic acid and mixed xylenes to give 16.5 g which in turn was sublimed at 190° (25-50 mmHg) to a golden sublimate of 7, mp 275-277°C; mass specturm (70 eV) m/e 252. The ^{1}H NMR spectrum was reproduced in EPA-600/2-78-006.

The tetracarboxylic acid 26b and is dianhydride 26a both serve as starting materials for preparation of perylene 20a. The results of several decarboxylation experiments are presented in Table 3.

Table 3 - Formation of Perylene from 26a and 26b



26a 7 26b

	% Yield		% Yield
[a] Soda lime, Zn dust, Δ	55-63	[i] Soda lime, Zn dust, Δ	60
[b] Soda lime, Δ	59-60(80)	[j] Soda lime, Δ	20
[c] Zn (Cu), Δ	20	[k] Soda lime, Zn (Cu), Δ	48
[d] Cu_2O, quinoline at reflux	12		
[e] Cu_2O in excess quinoline at reflux	12		
[f] Cu powder, $Ba(OH)_2 \cdot 8H_2O$ in refluxing dimethylnaphthylene	3		
[g] Kolbe electrolysis in methanol and KOH	0		
[h] Pd/C in refluxing methylnaphthalene in H_2 or N_2 atmosphere	0		

Conversion of Diene 20 to Anhydride 21 (Scheme I)

The synthesis of diene 20, Scheme I, is an adaptation of a published procedure.[21] This diene is prepared as follows: 1-tetralone (146 g, 1.0 mol) and 5.1 g of mercuric chloride were added to a 3-l., 2-neck, round-bottom flask (equipped with nitrogen inlet, reflux condenser, magnetic stirring, and heating mantle) containing 1400 mL of anhydrous benzene, 100 mL of anhydrous ethanol and 51.4 g (2 g atom) of aluminum foil. The system was flushed with nitrogen and then brought to reflux. After 20 hr, the liquid contents were decanted and washed twice with cold 10% HCl, and then with water. The organic phase was dried ($MgSO_4$), filtered, and concentrated through rotary evaporation. The resulting diol was then dissolved in a mixture of 300 mL of acetic acid and 300 mL of acetic anhydride. This solution was heated at reflux for 5 hr and then concentrated under vacuum to give 88 g (68%) of the diene 20, mp 135-137.5°.

The diene product 20 from above was then treated with 10 molar equivalents of maleic anhydride at 120° for 8 h, to give the Diels-Alder product which was isolated by dissolving the cooled reaction mixture in hot acetic acid, from which it crystallized to give 163 g (84%) of adduct 21, mp 234-252°C [lit. ^{21}mp 254°C].

Conversion of Anhydride 21 to Benzo[*ghi*]perylene (1) (Scheme I)

An intimate mixture of 12.1 g of 21 and 2.2 g of 10% Pd/C was placed in a 2 neck, 500 mL flask equipped with a gas inlet and condenser. After flushing with N_2, the flask was heated in a sand bath to 260-280°C for 8 hours. The resulting solid was broken up with hot toluene and placed on a Soxhlet column[1] charged with basic alumina. The hydrocarbon was eluted with refluxing toluene to give 8.8 g (94%) of light yellow 1, mp 273-276°C. [lit.[22] mp 273°C].

Conversion of Benzo[*ghi*]perylene (1) to Coronene-1,2-dicarboxylic anhydride (22) (Scheme I)

Benzo[*ghi*]perylene (1) (EPA-600/2-78-006) (1.85 g), chloranil (7.3 g), and maleic anhydride (22.6 g) were placed in a 300 mL flask equipped with condenser and magnetic stirrer. The mixture was refluxed for 6 h. Hydrogen chloride evolved and a dark precipitate deposited. After cooling, 30 mL of nitrobenzene were added and the suspension was gently warmed, filtered and the filter cake was washed with nitrobenzene and ether. The residue was recrystallized from 60 mL nitrobenzene to give 2.5 g reddish brown solid. The solid was placed in a Soxhlet extractor[1] containing neutral alumina and then extracted with refluxing benzene to remove excess chloranil. The remaining brown residue and the top layer of alumina were transferred to a sublimation apparatus.[20] Sublimation yielded red-orange crystals of 22 (1.5 g, 61%) which began to sinter at 455°C and melted at 499-500°C.

Fractional Sublimation of Coronene-1,2-dicarboxylic Anhydride (22) (Scheme I)

Into a 250 mL flask, equipped with receiver and two-way stopcock, was placed 20.8 g (0.056 mol) of anhydride 22. The system was alternately evacuated and flushed with argon. Using the reaction flask and the high temperature sand bath shown in Appendix C, benzo[*ghi*]perylene and other volatile impurities were sublimed away from anhydride 22 at 250-400°C (0.2 mmHg) during 4 h. After cooling, the receiver was replaced and the system evacuated and flushed with argon (4x). The flask was again heated using the high-temperature sand bath to 470-490°C (0.2 mmHg). The bulk of the anhydride sublimed suddenly at 490° giving 202 g (97%) of bright red-orange crystals of 22, mp $>$ 505°C, [lit.[23] mp 490-503°C]. TLC studies showed absence of 1. However, traces of 4 were observed.

Preparation of Coronene (4) from Anhydride 22 (Scheme I)

A 4.0 g (0.01 mol) sample of anhydride 22 and 10 g soda lime were thoroughly mixed with a mortar and pestle. This mixture was placed in the bottom of the reaction flask of Appendix C and covered with a 6 g layer of powdered soda lime and then 35 g of 4-8 mesh soda lime particles. Glass wool was then placed above the reactants. The system was alternately evacuated and flushed with argon (4x). Upon heating to 350-400°C (0.05 mmHg), 4 sublimed above the glass wool. This sublimate was placed in a Soxhlet apparatus[1] charged with Merck, activity I, basic alumina. The alumina was contained as a 5 cm diameter x 6 cm volume. The hydrocarbon was eluted with refluxing toluene to give a suspension of 4. Cooling and filtering gave 2.4 g (80%) of 4 as bright yellow fluffy needles, mp 434-438°C uncor.

Purification of Coronene 4 (Scheme I)

The combined product of 8 reactions (16.2 g) was placed in a Soxhlet apparatus[1] charged with basic alumina and then eluted with refluxing toluene. The resulting solution was filtered to give 15.0 g. Vacuum-sublimation gave 14.4 g, mp 437-440°C uncor. [lit.[25] mp 440°C]. Coronene 4 was not sufficiently soluble to yield a satisfactory NMR spectrum and the mass spectrum was used instead for identification. The mass values are presented in Table 4.

HPLC analysis with Waters liquid chromatograph using a 254nm UV detector, and a (3.0 mm x 30 cm) C_{18}-μ-Bondapak column with acetonitrile solvent (1mL/min) showed the purity of 4 to be 99.85%.

TABLE 4. MASS SPECTRAL DATA FOR CORONENE

PEAK NO.	MEASURED MASS	NO. POINTS	ABSOLUTE INTENSITY	% INT. BASE	% INT. NREF	% TOT. ION
1	405	7	24.	0.0	0.0	0.0
2	314	12	47.	0.0	0.0	0.0
3	303	16	65.	0.1	0.1	0.1*
4	302	61	1761.	3.1	3.1	1.5*
5	301	2	14612.	25.9	25.9	12.5*
6	300	9	56408.	100.0	100.0	48.3*
7	296	7	25.	0.0	0.0	0.0
8	266	8	27.	0.0	0.0	0.0
9	244	7	17.	0.0	0.0	0.0
10	242	7	32.	0.1	0.1	0.0
11	240	9	24.	0.0	0.0	0.0
12	230	14	60.	0.1	0.1	0.1*
13	226	11	32.	0.1	0.1	0.0
14	220	7	20.	0.0	0.0	0.0
15	218	7	25.	0.0	0.0	0.0
16	216	10	41.	0.0	0.0	0.0
17	207	7	23.	0.0	0.0	0.0
18	195	7	27.	0.0	0.0	0.0
19	174	8	23.	0.0	0.0	0.0
20	151	11	74.	0.1	0.1	0.0*
21	150	62	3409.	6.0	6.0	2.9
22	115	21	92.	0.2	0.2	0.0*
23	114	13	76.	0.1	0.1	0.0*
24	101	9	38.	0.0	0.0	0.0
25	100	56	1045.	1.9	1.9	0.9*
26	96	8	24.	0.0	0.0	0.0
27	94	7	26.	0.0	0.0	0.0
28	83	7	25.	0.0	0.0	0.0
29	82	42	463.	0.8	0.8	0.4*
30	78	28	167.	0.3	0.3	0.1*
31	60	10	49.	0.0	0.0	0.0*
32	59	61	1728.	3.1	3.1	1.5
33	58	3	36314.	64.4	-	31.1*

DP0:COROA.MS
SCAN: 1, 8/21/79 15: 5

NO. PEAKS: 33
BASE/NREF INT: 56408./ 56408.
TIC: 116823.
MASS RANGE: 58 - 405
RETN TIME/MISC: 0: 0/ 0/ 0/ 0

Benzo[*e*]pyrene (2), 1,2,3,6,7,8-Hexahydropyrene (5) and 4,5,9,10-Tetrahydropyrene (9) (Scheme 2)

Hydrocarbons 2, 5, and 9 were synthesized as shown in Scheme 2.

Pyrene was reduced through catalytic hydrogenation (see Figure 1 for composition) which is a good route to 9 but less useful for the preparation of 5 needed to prepare 2. To produce 5 in adequate quantity for synthesis of 2, we studied reduction of pyrene with sodium in a variety of alcohols and amines.[24]

Hydrogenation of Pyrene to 4,5,9,10-Tetrahydropyrene (9) (Figure 1)

Pyrene (100 g, 0.5 mol), previously desulfurized, was catalytically hydrogenated in a Parr apparatus in 1.5 L HOAc with 8 g 5% Pd/C at 60 psig and ca. 55°C. Maximum GC yields, 85-91%, were observed at reaction times ranging from 30-45 h. The reaction was stopped, cooled, and filtered through Dicalite to remove the catalyst. The solution was concentrated and the residue taken into ether (1 L) which was washed with saturated Na_2CO_3 (1 L) and H_2O (1 L). The organic phase was dried ($MgSO_4$), filtered and concentrated to give 95 g of 9, 95% pure. This product was recrystalized from ethyl acetate and then passed through a picric acid column[25]. Crystalization (ethyl acetate) gave 9, mp.140°C [lit.[26]138°C] in ca. 80% overall yield. IR (KBr) 3050 (ArH)cm^{-1}; ^1H NMR ($DCCl_3$) δ 2.82 (s, 8, $ArCH_2$), 7.02 (s, 6, ArH); ^{13}C NMR ($DCCl_3$) ppm 28.17 (CH_2), 125.57, 125.65, 126.68, and 135.02 (aromatic C).

Reduction of Pyrene with Sodium and n-Pentanol

Pyrene (200 g, 1.0 mol) was reduced with 180 g (7.8 g-atom) Na in 4.5 L n-pentanol at reflux. GC analysis of the final product indicated the reaction mixture contained 58% of 5. Crystallization from n-hexane afforded

99% pure 4b (106 g, 0.51 mol, 51% yield). The yield of 4b ranged from 35% to 58% (average 48%). When the amount of Na is increased or decreased the yield of 4b decreases sharply.

After removing crystals of 4b by filtration, the mother liquor was analyzed by GC-mass spectrometry[27] (glass capillary GC gave separation of some isomers not separated by the packed GC column used previously). The mother liquor contained 8 components in addition to 5.

Purification of 1,2,3,6,7,8-Hexahydropyrene (5) (Scheme 2)

n-Hexane was percolated through a Soxhlet column containing ca. 250 g of 5 (99% pure) obtained by sodium-alcohol reduction of pyrene over a bed of picric acid (100 g) packed above basic alumina (100 g). Fractions were collected and analyzed by GC. The purest fractions (ca. 200 g, 99.5% pure) were chromatographed on a dual column of basic alumina (100 g) above silica gel (150 g). Fractions were collected and 5 was allowed to crystallize and filtered. These crystals (mp 133-134°, lit.[23] 132-133.5°C) were analyzed by GC and all those exceeding 99.9% purity were combined and zone refined. Less pure fractions were combined and reprocessed in a similar manner. IR (KBr) 3050 (ArH) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.84-2.10 (pentet, J = 6Hz, 4, $ArCH_2\underline{CH_2}$), 2.92-3.04 (t, J = 6Hz, 8, $ArCH_2$), 7.02 (s, 4, ArH); ^{13}C NMR ($CDCl_3$) ppm.

β-(1,2,3,6,7,8-Hexahydro-4-pyrenoyl) propionic acid (28) (Scheme 2)

Sym-hexahydropyrene (5), (85 g, 0.41 mol) and succinic anhydride (42 g, 0.41 mol) were dissolved in 1400 mL nitroethane under nitrogen in a 3 L flask. The solution was cooled with an ice bath and aluminum chloride (115 g, 0.88 mol) was added in 35 min. to produce an orange-red solution. The ice bath was removed and the solution stirred 42 h. The solution was added to deionized water (700 mL) and extracted with toluene

(2 x 1 L). The toluene extracts were combined, dried ($MgSO_4$), filtered, and concentrated by rotary evaporation to give 110 g (0.36 mol, 87% yield of 28, mp 173-6°, [lit.[24] 173.5°] IR (KBr) 3600-2800 ($-CO_2H$), 1710 ($-\overset{O}{\overset{\|}{C}}-OH$), 1690 (ArC=O)$cm^{-1}$; ^{1}H NMR ($CDCl_3$) δ 1.86-2.16 (m, J = 6Hz, 4, $ArCH_2CH_2$), 2.74-2.86 (t, J = 6Hz, 2, CH_2CO_2H), 2.9-3.3 (m, 10, $ArCH_2$ and $ArC(O)CH_2$), 7.16 (s, 2, ArH), 7.34 (s, 1, Ar(H)C=O), 8.1-8.6 (s-broad, 1, CO_2H); ^{13}C NMR ($CDCl_3$) ppm 23.0, 23.1, 28.4, 29.0, 29.1, 31.3, 31.5, and 36.9 (aliphatic C), 121.6, 124.4, 125.3, 130.1, 131.1, 132.7, 133.9, 134.0, 134.7, and 136.0 (aromatic C), 178.6 (CO_2H), 202.9 (C=O); MS m/z (rel. intensity).

δ-(1,2,3,6,7,8-Hexahydro-4-pyrenyl)butanoic acid (29) (Scheme 2)

Zn(Hg) amalgam was prepared by adding 3.6 g $HgCl_2$, 3.6 mL conc. HCl, and 75 ML H_2O (deionized) to 66 g mossy zinc. After stirring the mixture 15 min., the supernatant liquid was decanted. The resulting Zn(Hg) amalgam was placed in a 3 L flask containing 43 g (0.14 mol) ketoacid 28 130 mL toluene, 170 mL dionized water, and 120 mL conc. HCl. The mixture was stirred (mechanically) and refluxed 72 h while adding 20 mL conc. HCl every 4 h. The mixture was cooled, filtered, and extracted. The aqueous layer was extracted with ethyl-ether (100 mL). The organic layers were combined, dried ($MgSO_4$), filtered, and concentrated to afford 32 g (0.12 mol, 83%) of the desoxyacid 29 mp 132° [lit.[28] 133-4°C]; IR (KBr) 3550-2800 (CO_2H), 1710 (C=O)cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.8-2.2 (m, 6, $ArCH_2CH_2$), 2.3-2.8 (m, 4, $ArCH_2CH_2CH_2CO_2H$), 2.9-3.1 (t, J = 10Hz, 8, ArCH2), 6.95-7.15 (m, 3, ArH); ^{13}C NMR ($CDCl_3$) ppm.

9-Oxo-1,2,3,6,7,8,9,10,11,12-decahydrobenzo[e]pyrene (30)(Scheme 2)

Acid 29 (18 g, 0.061 mol) was added to 300 g polyphosphoric acid (PPA in a 500 mL flask equipped with good mechanical stirrer. The mixture was stirred and heated to 140°C for 2.5 h. It was cooled and poured over ice. On hydrolysis

a greenish-yellow solid formed which was extracted into ethylether: toluene (100 mL:100 mL), dried ($MgSO_4$), filtered, and concentrated to give a dark tar. Distillation (Kugelrohr, 280°C, 0.6 mm) afforded 14.4 g (0.052 mol, 85.5%) of ketone 30 mp 144-6°C [lit.[28] 147-8°C]: IR (KBr) 1680 (>C=O)cm^{-1}; ^1H NMR ($DCCl_3$) δ 1.90-2.14 (pentet, J=6Hz, 6, $ArCH_2C\underline{H}_2$), 2.62-2.76 (t, J=6Hz, 2, $ArC\underline{H}_2$), 2.85-3.10 (m, 8, $ArC\underline{H}_2$), 3.40-3.54 (t, J=7Hz, 2, $ArC(O)C\underline{H}_2$), 6.98-7.18 (2xd, 2, Ar$\underline{H}$); ^{13}C NMR ppm 22.4, 22.9, 23.6, 27.3, 28.0, 30.5, 31.1, 31.4, and 41.2 (aliphatic C), 123.2, 125.8, 127.9, 128.9, 130.1, 131.7, 133.3, 134.9, 136.6, and 139.0 (aromatic C), 201.4 (C=O); MS m/z (rel. intensity) $M+1^+$ 277(21.6), M^+ 276(100), 261(22.4), 220(18.7), 205(18.6), 203(14.3), 202(16.6), 101(15.2).

9-Hydroxy-1,2,3,4,5,6,7,8,9,10-decahydrobenzo[e]pyrene (31a) Scheme 2)

Ketone 30 (14.0 g, 0.05 mol) was placed in a 2 L flask containing 1 L ethanol. The solution was stirred (magnetically) under N_2 and 14 g (0.37 mol) $NaBH_4$ was added in 25 min. After stirring 24 h at room temperature, the mixture was concentrated by rotary evaporation, dissolved in 500 mL toluene, and washed with deionized water (600 mL). The toluene extract was dried ($MgSO_4$), filtered, and concentrated to afford 12.8 g (0.046 mol, 92.1%) of alcohol 31a, mp 152-4°C. IR (KBr) 3225 (OH)cm^{-1}; ^1H NMR 1.8-2.5 (m, 8, aliphatic), 2.8-3.6 (m, 11, benzylic), 5.32 (s, 1, O$\underline{H}$), 7.3 (s, 2, Ar$\underline{H}$); ^{13}C NMR ($DCCl_3$) ppm 16.84, 22.99, 23.16, 26.90, 27.29, 27.54, 31.16, and 31.45 (aliphatic and benzylic $\underline{C}H_2$), 64.46 ($\underline{C}OH$), 122.53, 123.28, 128.57, 129.44, 130.26, 130.99, 131.58, 133.24, 133.38, and 134.11 (aromatic); MS m/z (rel. intensity) $M+1^+$-18 261 (21.3), M^+ -18 260(100), 259(14.2), 245(16.1), 232(15.1), 231(17.0), 215(15.8), 108(24.7).

1,2,3,6,7,8,9,10-Octahydrobenzo[e]pyrene (31b) (Scheme 2)

Alcohol 31a (2.3 g, 8.3 mmol) was heated at 90°C for 2 h in 70 mL HOAc and 3 drops conc. HCl with magnetic stirring. It was concentrated by rotary evaporation. The residue was dissolved in ether and washed with H_2O. The organic phase was dried ($MgSO_4$), filtered, and concentrated to afford 2.2 g of 31b, mp 123-6°C, [lit.[28] 129-130°C] as a yellow crystalline solid. IR (KBr) 3025 (C=C-H) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.86-2.12 (pentet, J = 6Hz, 4, $-CH_2-$ at positions 2 and 7), 2.20-2.40 (q, J = 7Hz, 2, C=C-CH_2), 2.78-3.10 (m, 10, ArCH_2), 6.05-6.24 (m, 1, ArCH=CH), 6.72-6.94 (d, J = 22Hz, 1, ArCH=C), ^{13}C NMR ($CDCl_3$) ppm 23.0, 23.2 (2 carbons), 24.5, 27.3, 27.7, and 31.4 (2 carbons) - (aliphatic C). 122.7, 123.1, 124.9, 127.5, 127.8, 129.0 (2 carbons), 129.5, 129.7, 133.6, 134.2, and 148.7 (aromatic and vinyl C). MS m/z (rel. intensity) $M+1^+$ 261 (21.9), M^+ 260 (100), 259 (13.9), 245 (15.9), 232 (15.2), 231 (16.9), 215 (15.5), 108 (24.7).

Benzo[e]pyrene 2 (Scheme 2)

Alcohol 31 (21.9 g, 0.079 mol) was placed in a 200 mL flask with 2 g of 10% Pd/C. The neat mixture was dehydrogenated at 290°C under N_2 in a salt bath. After heating 48 h, the mixture was cooled and percolated through a column containing 10 g neutral alumina over 10 g silica gel using toluene as solvent. The yellowish compound (20.0 g) had mp 150°C [lit.[24] 178-180°C]. This was percolated through 15 g basic alumina over 15 g silica gel to afford 19.5 g (0.077 mol, 98%) of hydrocarbon 2 mp 179-180°C. IR (KBr) 3050(ArH)cm^{-1}; ^1H NMR ($DCCl_3$) δ 7.60-7.70 (2xd, J=3Hz, 2, $C_{10}H$ and $C_{11}H$), 7.84-8.12 (m, 6, ArH), 8.68-8.82 (m, 4, ArH-bay regions); ^{13}C NMR ($DCCl_3$) ppm. MS m/z (rel. intensity) $M+1^+$253(21), M^+252(100), 251(5), 250(21), 126(25), 125(35), 113(14), 112(8).

1,2,3,4-Tetrahydroanthracene (8) (Scheme 3)

Hydrocarbon 8 was prepared by selective hydrogenation of anthracene in acetic acid with rhodium catalyst supported on carbon. Optimum yields were obtained at ca. 1 psi hydrogen in refluxing acetic acid,[10a] although good yields were obtained in a Parr shaker at 10 and 30 psi and 60°C. In the former reaction, 8 was obtained in 80 to 90% yield, and in the latter reactions, about 75% yield. The reaction was monitored by GC until an acceptable conversion was observed and was then stopped. Prolonged hydrogenation resulted in sym. octahydroanthracene as the major product.

After removing the acetic acid, the reaction mixture was placed on a column of picric acid in a Soxhlet extractor[1,25] and then eluated with isohexane. The hydrocarbons which do not form picrates (dihydroanthracene and octahydroanthracene) elute while 8 and anthracene are retained. A fraction was taken and then the picrate-forming compounds were eluted with fresh isohexane. This fraction was stripped of isohexane and refluxed in toluene with maleic anhydride for 2 hr. Toluene was stripped and the reaction mixture was eluted through a basic alumina column with isohexane. The mixture eluted was recrystallized from isohexane to give 8, > 99.9% pure.

To attain 8 with impurities of less than 0.1%, two passes through the picric acid column and two treatments with maleic anhydride were required. A final crystallization from isohexane gave 8 at 99.99% purity (GC). When this fraction was distilled (Kugelrohr apparatus at 102-108°C, 2 mmHg) to remove traces of solvent, a small amount of 8 was converted to anthracene to give a final product of > 99.9% of 8 and 0.02% anthracene. Hydrocarbon

8 is sensitive to air oxidation and rapidly deteriorates in solution when exposed to light and air.

An alternate preparation[11] of 8 was achieved as shown in Scheme 3 using KOH·NaOH. The yield of 8 was 74%.

1,10-Trimethylenephenanthrene (10) (Scheme 4)

Hydrocarbon 10 was prepared by the previously described HI-P_4 reduction of benzanthrone.[12] It was eluted through alumina (dual acidic and basic) with n-hexane in a Soxhlet column.[1] After removal of n-hexane solvent, the picrate of 10 was formed in alcohol solution. Two recrystallizations from ethanol gave an orange picrate, mp 123-124°. This picrate was decomposed by elution with isohexane through basic alumina.[25] Concentration of the solvent and distillation using a Kugelrohr apparatus gave 10, mp 80.5-81.0 °C.

Synthesis of 11H-Indeno[1,2-b]quinoline (15)(Scheme 5)

To a solution of 16 g (0.076 mol) of O-aminobenzaldehyde[13] and 17.5 g (0.076 mol) of 1-indanone in 100 mL of 95% EtOH was added 8 mL of conc. HCl. The red solution was warmed for 1 h then evaporated to 50 mL. The residue solidified after cooling and the solid was collected by filtration. The solid was rinsed with small portions of cold 95% EtOH until colorless. The crude hydrochloride salt was added to 250 mL of 0.8 M NaOH and heated to boiling. The solid was collected by filtration and dried giving 16 g of 11H-indeno[1,2-b]quinoline (15). The mother liquor from the condensation was concentrated and treated with base to give an additional 2 g of 15. Purification was accomplished by Soxhlet extraction[1] over basic alumina followed by sublimation; mp 167-169°C [lit.[29,30] 168-170°C].

Preparation of 2,2'-Dihydroxy-1,1'binaphthyl (38) from 2-Naphthol (37) (Scheme 6)

To 3 L of water heated to 90°C was added 250 g of 37 with vigorous stirring. Next, 84 mL of 30% aqueous $FeCl_3$ was added. The resulting precipitate was stirred 5 minutes and filtered while hot. The brown product was washed with 500 mL hot water and then air dried. This gave 142 g (73%) of product which was taken up in 10% NaOH and filtered. Upon acidification, the product was collected and dried. It was then placed in a Soxhlet extractor charged with acidic alumina (Merck, activity I), and 2,2'-dihydroxy-1,1'-binaphthyl (38) was eluted with refluxing benzene to yield colorless crystals, mp 214-216°C [lit.[15] mp 216°C].

Conversion of 2,2'-Dihydroxy-1,1'-binaphthyl (38) to Dinaphtho[2,1-b:1',2'-d]furan (17) (Scheme 6)

Into an open sublimation flask[20] was placed 25.4 g of 38 and 1.8 g V_2O_5. The flask was placed in a molten salt bath (160°C) and the temperature was rapidly raised to 210-230°C. These conditions were maintained for 8 h. Upon cooling, the black residue and yellow sublimate were treated with 10% NaOH. The alkali solution was decanted and the residue was broken up with hot toluene. A total of 26 g of base insoluble material was collected. Kugelrohr distillation at 140-160°C (0.3 mmHg) gave 19.0 g (80%) of yellow distillate. This product was placed in a Soxnlet extractor[1] charged with basic alumina (7 x 5.5 cm of Merck activity I). Elution with refluxing isohexane gave a solution which deposited 17.3 g of bright yellow crystals of 17, mp 154-155°C.

Purification of 17 (Scheme 6)

A 19.0 g sample of 17 was loaded, in three installments, onto columns of basic alumina (30 x 5 cm of Merck activity I) and eluted with a benzene:

isohexane mixture (1:2) to give 15.8 g of colorless crystals (mp 154.4-155.5°C). These crystals were loaded onto a Soxhlet column[1] charged with basic alumina (8.5 x 3.5 cm of Merck activity I) and then extracted for 4 h with refluxing n-hexane. The resulting solution, upon cooling, gave 12 g of colorless crystals. Upon distillation using an oil bath (185°, 0.2 mmHg), 11.1 g of 17 were collected, which melted at 156-157°C uncorr. [lit.[15] 156°C], MS m/e (rel. intensity) M^+ 268. HPLC analysis with a Waters liquid chromatograph using a 254 nm UV detector, (3.9 mm x 30 cm) u-Porasil column and ether-$CHCl_3$ (0.7 mL/min., retention time 4.5 min.) or isoctane (2 mL/min., retention time 12.5 min.) showed a single peak.

Conversion of 2,2'-Dihydroxy-1,1'-binaphthyl (38) to peri-Xanthenoxanthene (18) (Scheme 6)

To a 1 L flask was added an intimate mixture of 14.05 g (0.05 mol) of 38, 18.7 g CuO (freshly prepared and dried), and 20 mL nitrobenzene. This mixture was heated at a bath temperature of 250-275°C for 2 h. The bulk of the volatile material was distilled away from the solids (250°C at 15 mmHg). The bath temperature was increased to 260°C over a 2 h period. After cooling, the black solid was broken up with hot 10% HCl followed by hot toluene. All water insoluble solids were combined and any remaining solvent was evaporated. Nitrobenzene and any other volative products were distilled from the mixture at 190°C and 0.07 mmHg using a Kugelrohr apparatus.

Purification of peri-Xanthenozanthene (18) (Scheme 6)

Solids containing inorganic impurities and 1.7 g crude[1] 1 were broken up in hot toluene and added as a suspension to a Soxhlet extractor[1] charged with acidic alumina (3 cm x 5 cm diameter) over basic alumina (Merck activity I, 4 cm x 5 cm diameter). Peri-xanthenoxanthene was then

eluted with refluxing toluene to give a solution which deposited 11.2 g of 18. This procedure was repeated for the material from a second reaction giving a total of 22 g of 18.

The combined products were loaded on a Soxhlet extractor charged with acidic alumina (3 cm x 5 cm diameter) and basic alumina (Merck activity I, 6 cm x 5 cm diameter). Elution with refluxing toluene gave a solution which yielded a first crop of crystals, 18.5 g. These crystals were loaded on a Soxhlet extractor[1] charged with basic alumina (Merck activity I, 9.5 cm x 6 cm diameter). Refluxing isooctane (bp 99°C) was eluted through this column for 24 h to remove dinaphthofuran and other impurities. Peri-xantheno-xanthene was next eluted with refluxing benzene. After cooling, the resulting benzene extract gave 12.3 g of fluffy yellow crystals. The crystals were placed in a distillation flask and alternately flushed with argon and evacuated.

Material volatile below 250°C/0.15 mmHg was distilled away and the receiver was changed. The system was again evacuated and flushed with argon. The fraction distilling at sand bath temperatures between 250-300°C (0.15 mmHg) was collected, to give 9.8 g of yellow peri-xanthenoxanthene, mp 241-2°C (uncorr.) [lit.[31] mp 240°C].

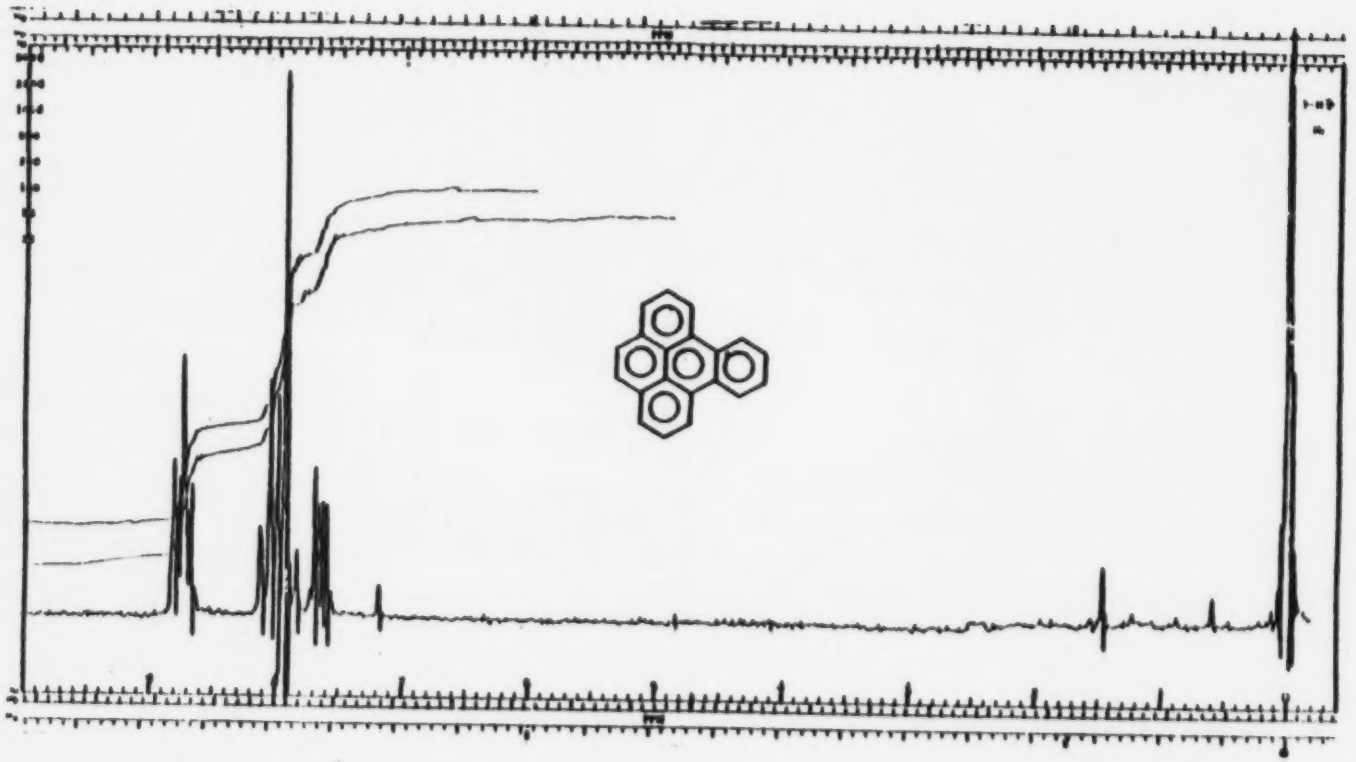


Figure 3. ^{1}H NMR Spectrum of Benzo[e]pyrene (3) at 100 MHz in $CDCl_3$.

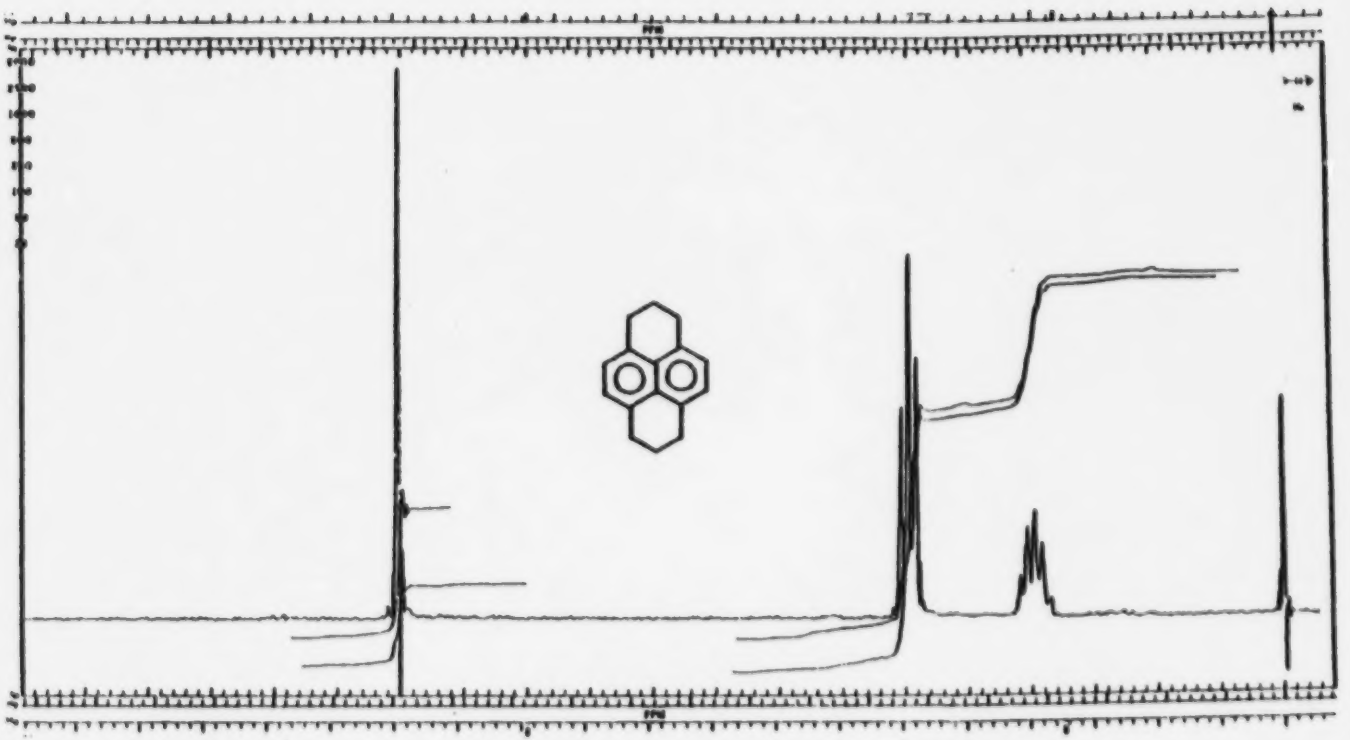


Figure 4. ^{1}H NMR Spectrum of 1,2,3,6,7,8-Hexahydropyrene (5) at 100 MHz in $CDCl_3$.

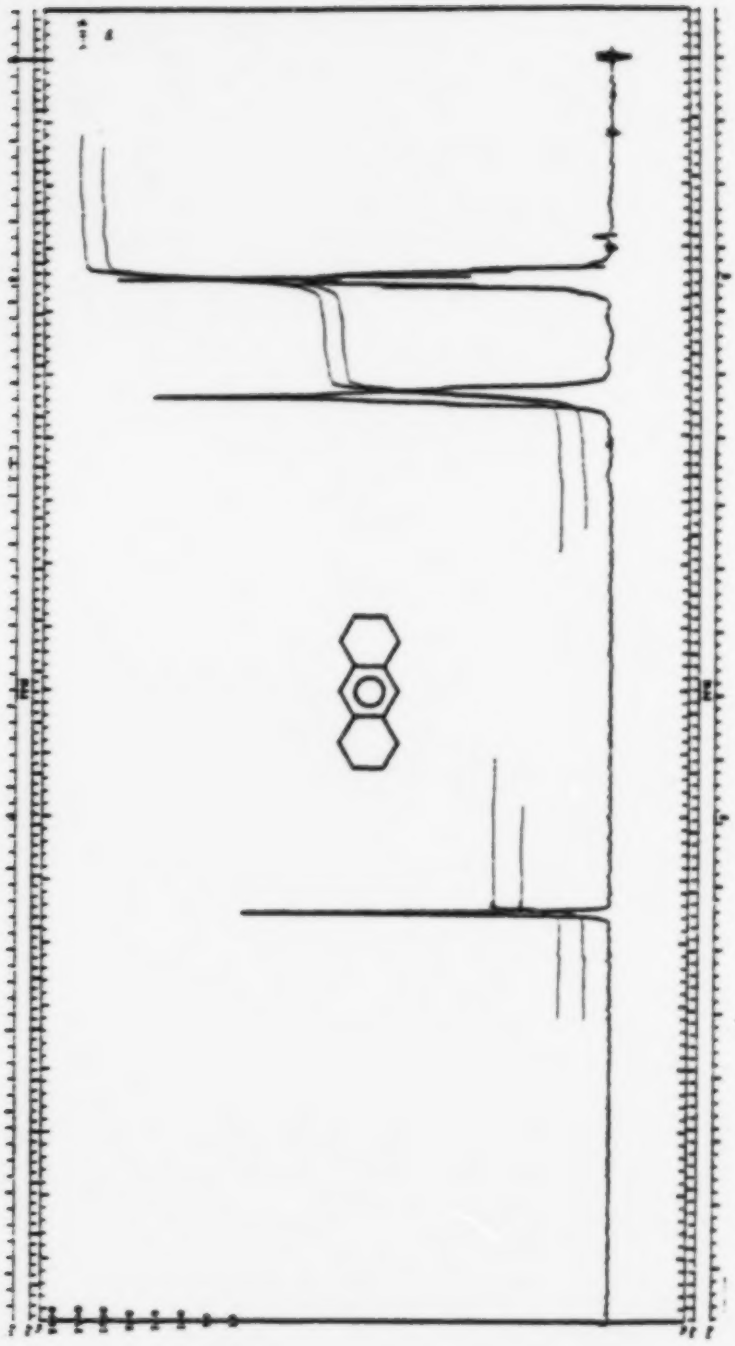


Figure 5. ^{1}H NMR Spectrum of sym-Octahydroanthracene (6) at 100 MHz in $CDCl_3$.

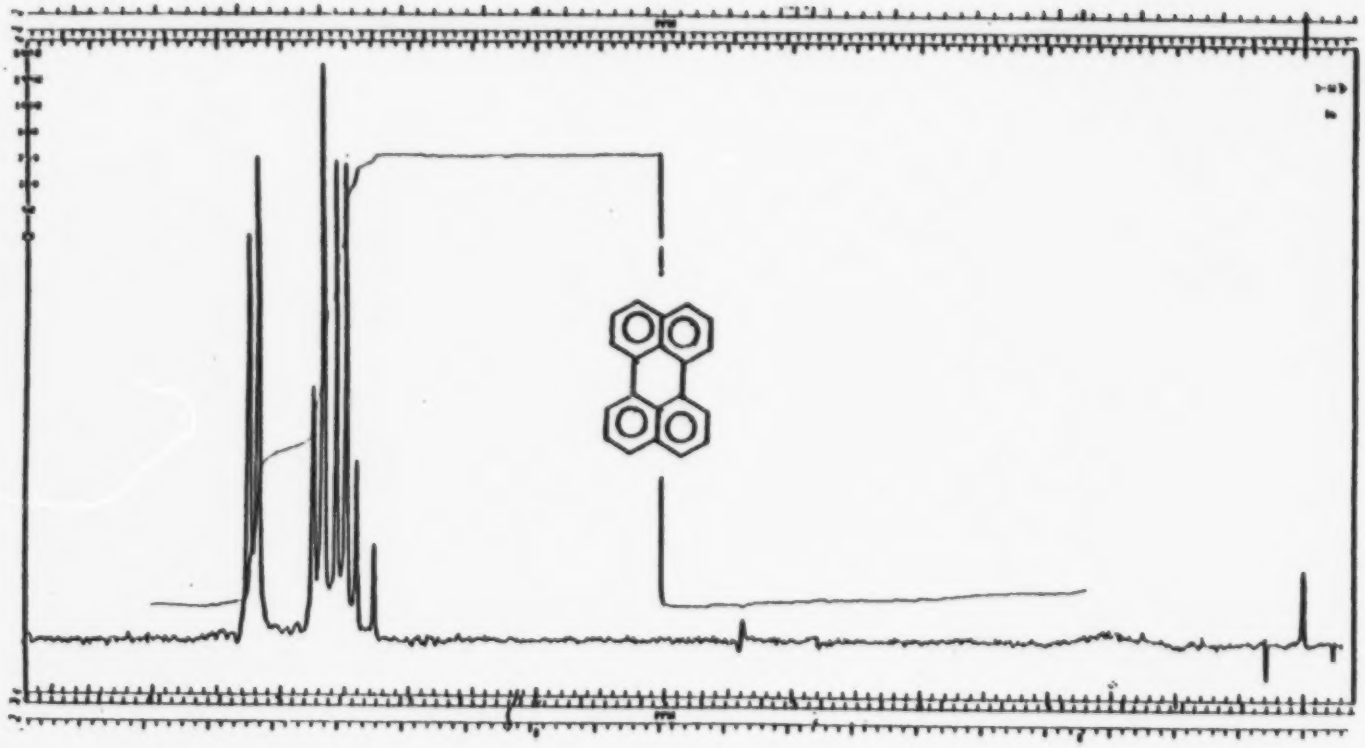


Figure 6. ^{1}H NMR Spectrum of Perylene (7) at 100 MHz in $CDCl_3$.

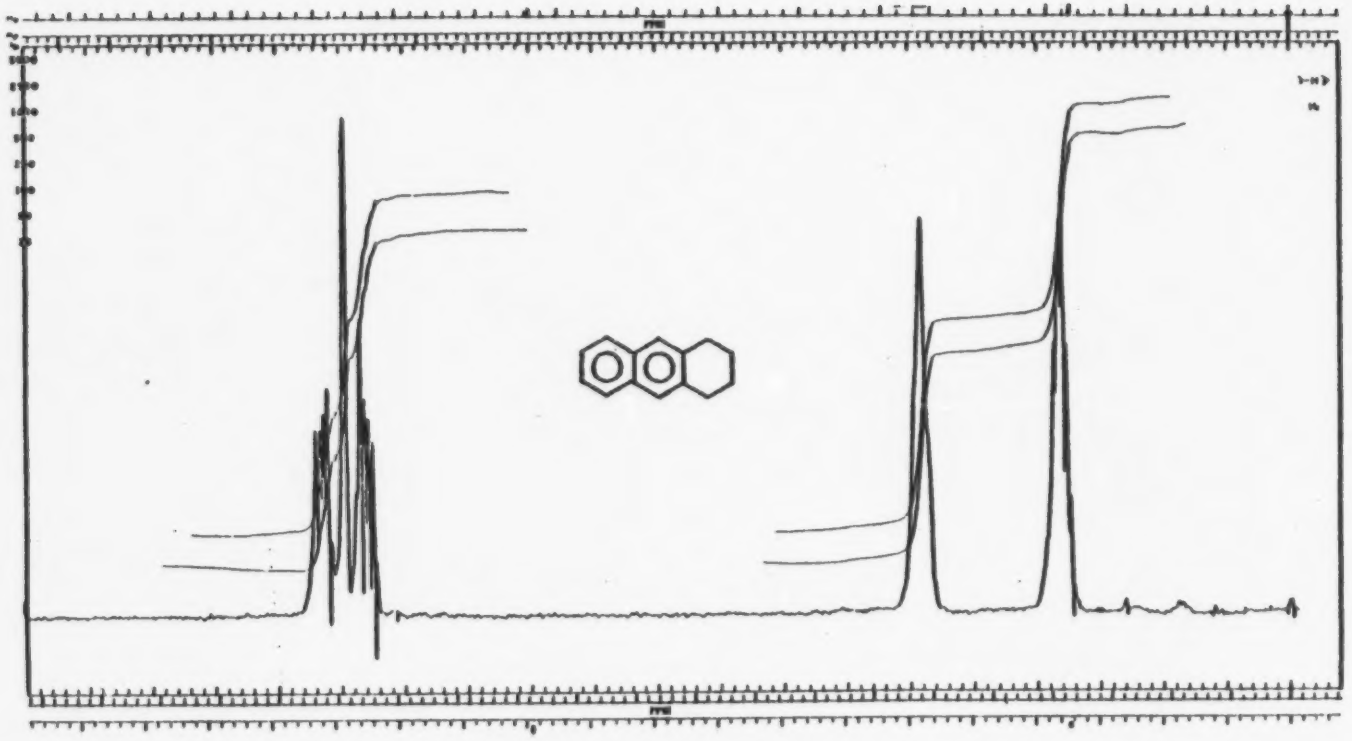


Figure 7. ^{1}H NMR Spectrum of 1,2,3,4-Tetrahydroanthracene (8) at 100 MHz in $CDCl_3$.

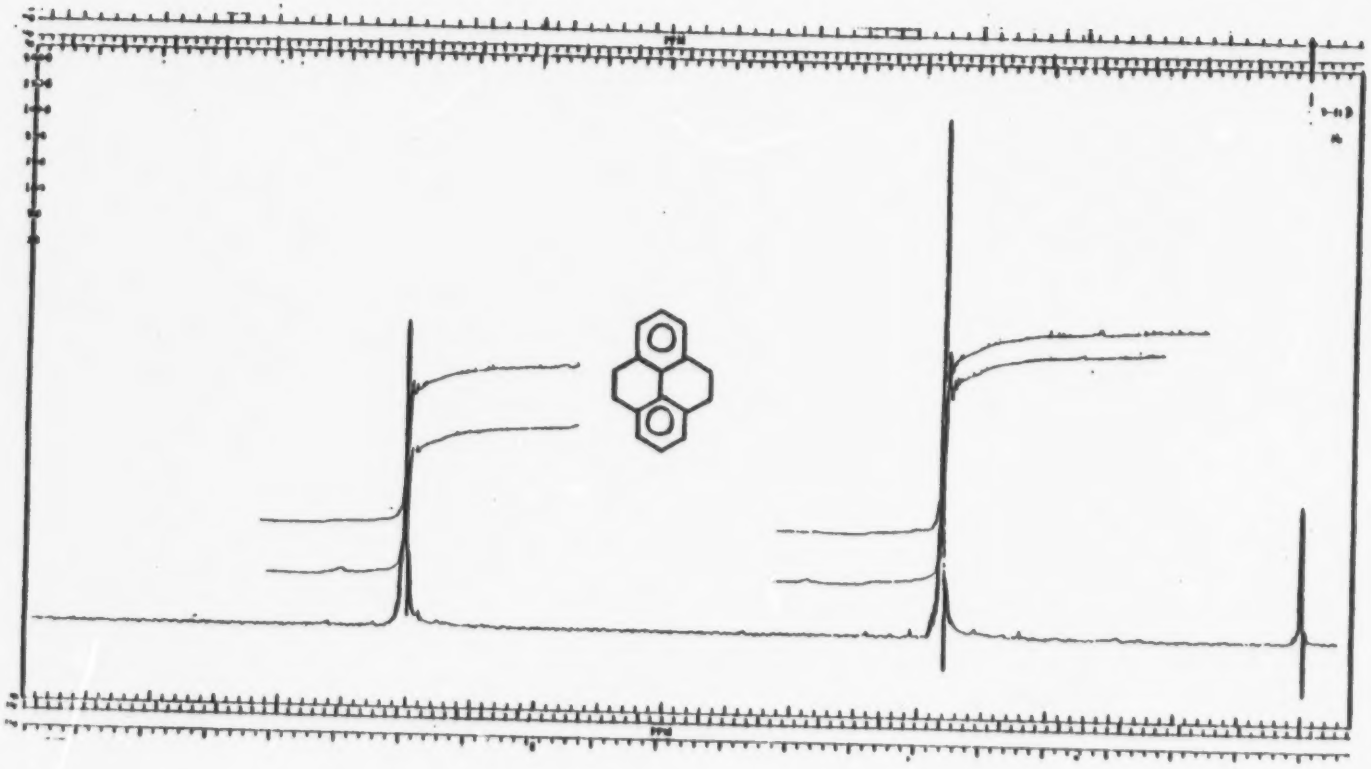


Figure 8. ^{1}H NMR Spectrum of 4,5,9,10-Tetrahydropyrene (9) at 100 MHz in $CDCl_3$.

Figure 9. ^{1}H NMR Spectrum 1,10-Trimethylenephenanthrene (10) at 100 MHz in $CDCl_3$.

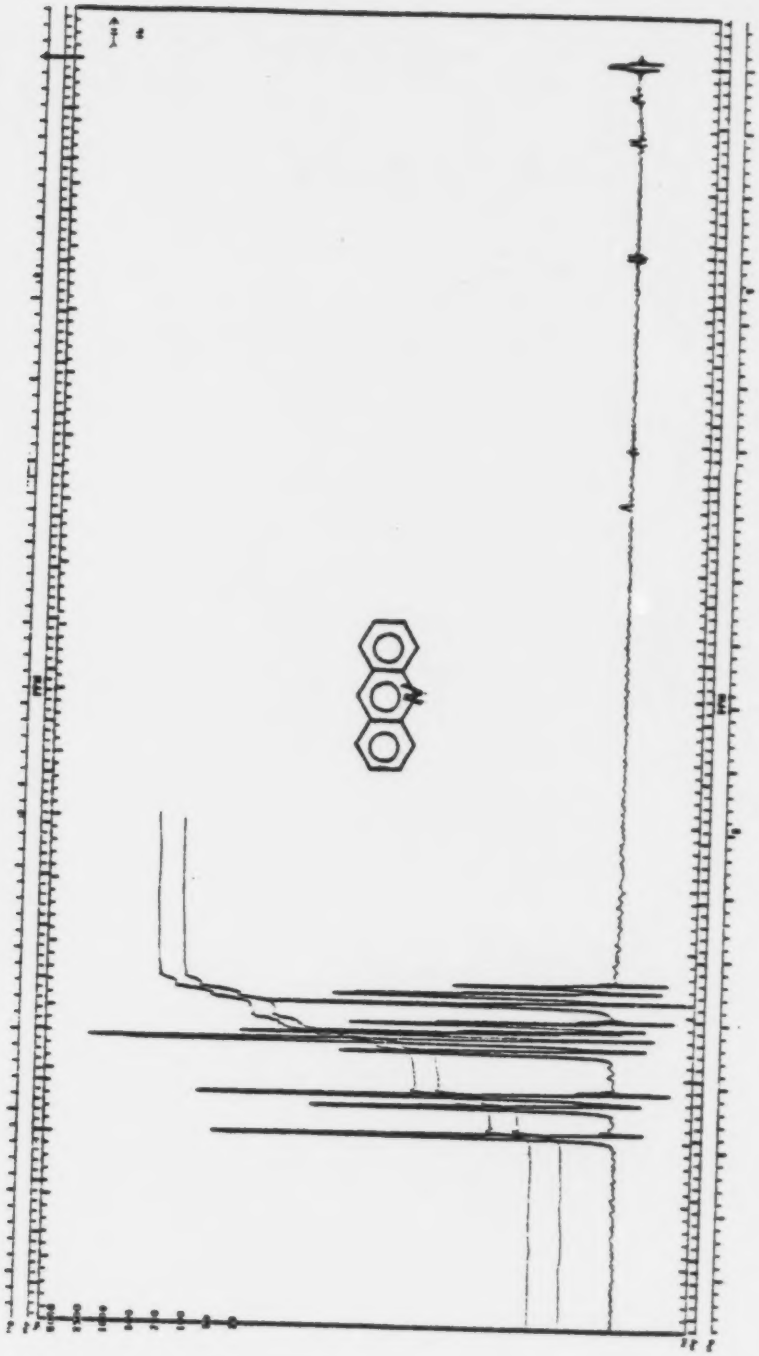


Figure 10a. ^{1}H NMR Spectrum of Acridine (11) at 100 MHz in $CDCl_3$.

Figure 10b. ^{13}C NMR Spectrum of Acridine (11) in $CDCl_3$.

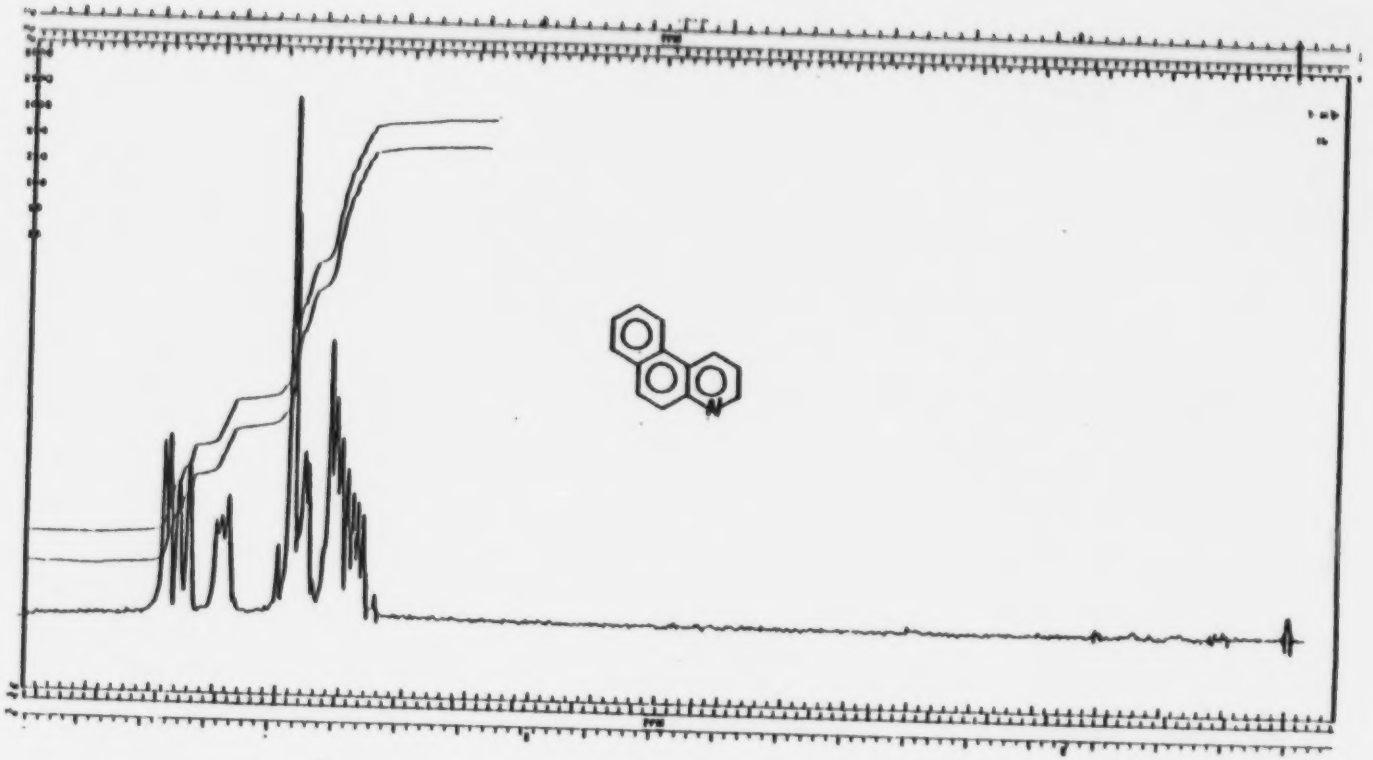


Figure 11a. ^{1}H NMR Spectrum of Benzo[f]quinoline (12) at 100 MHz in $CDCl_3$.

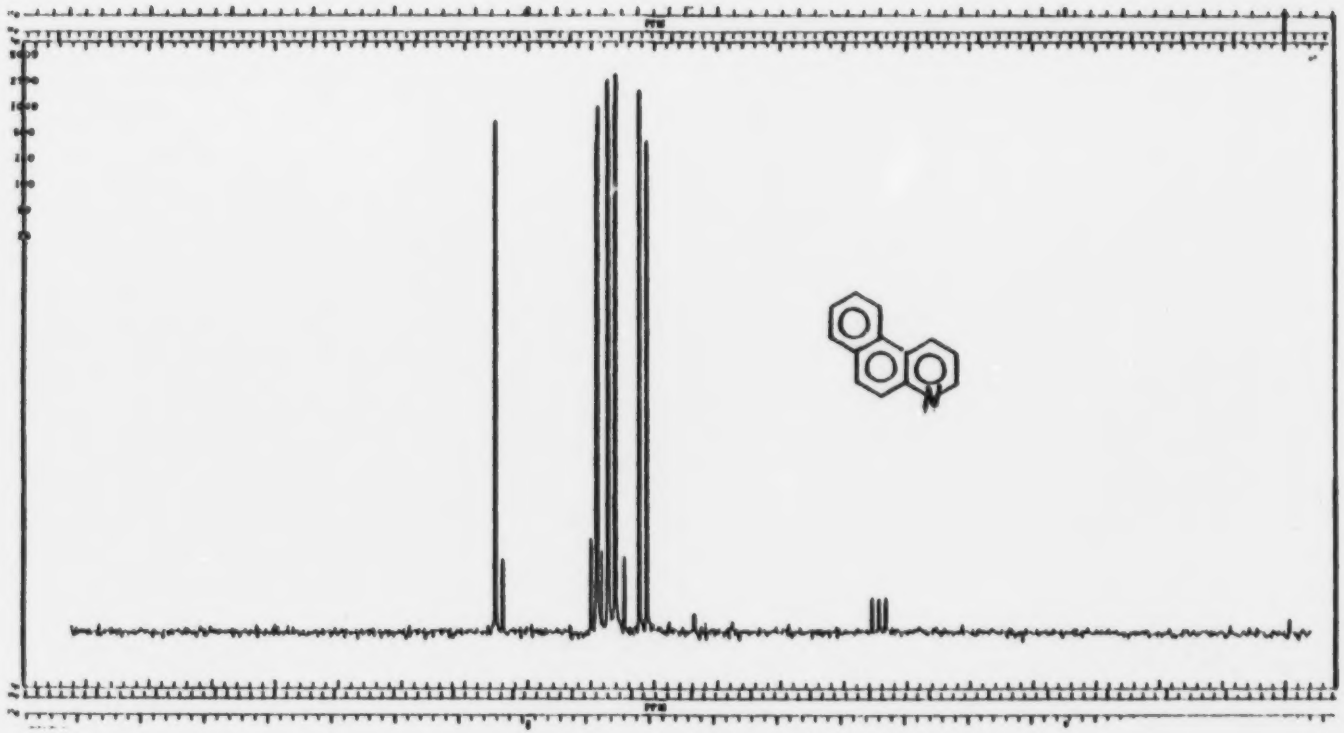


Figure 11b. ^{13}C NMR Spectrum of Benzo[f]quinoline (12) in $CDCl_3$.

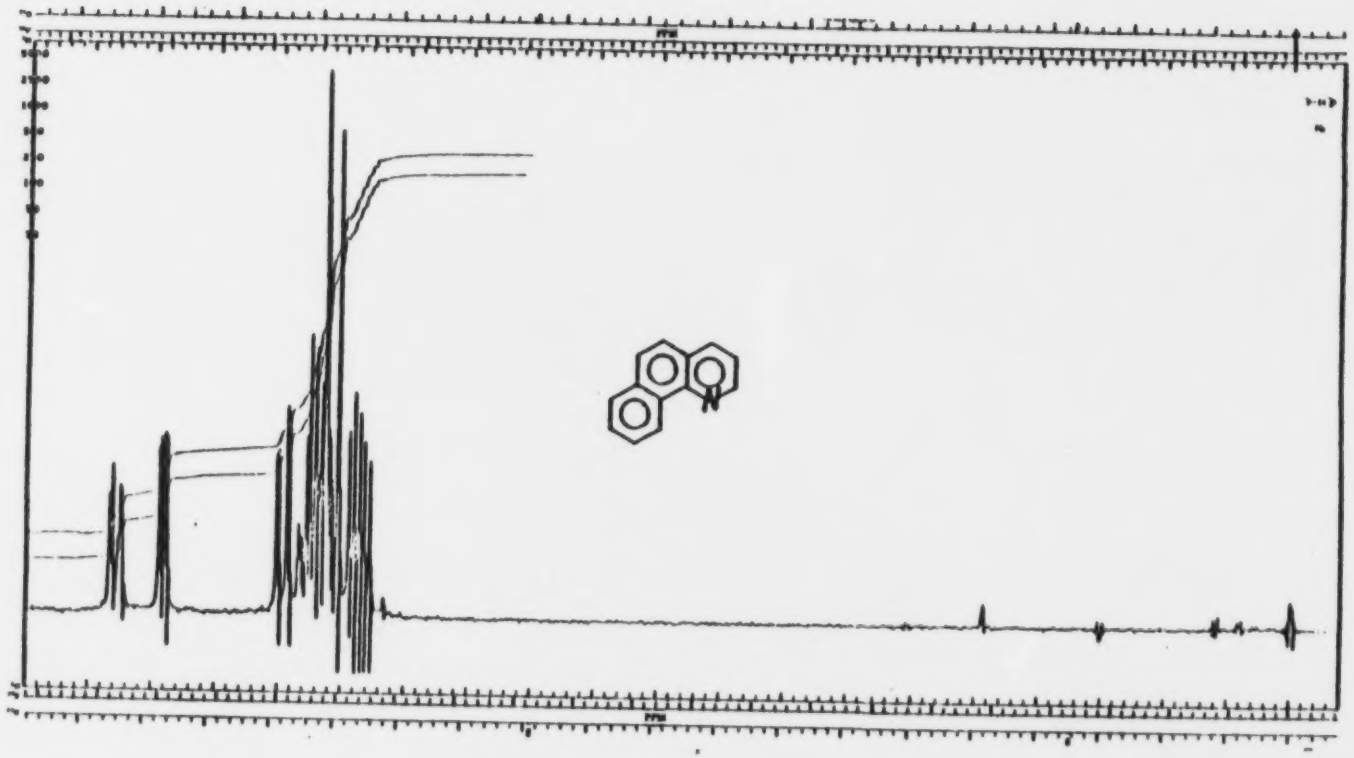


Figure 12a. ^{1}H NMR Spectrum of Benzo[h]quinoline (13) at 100 MHz in $CDCl_3$.

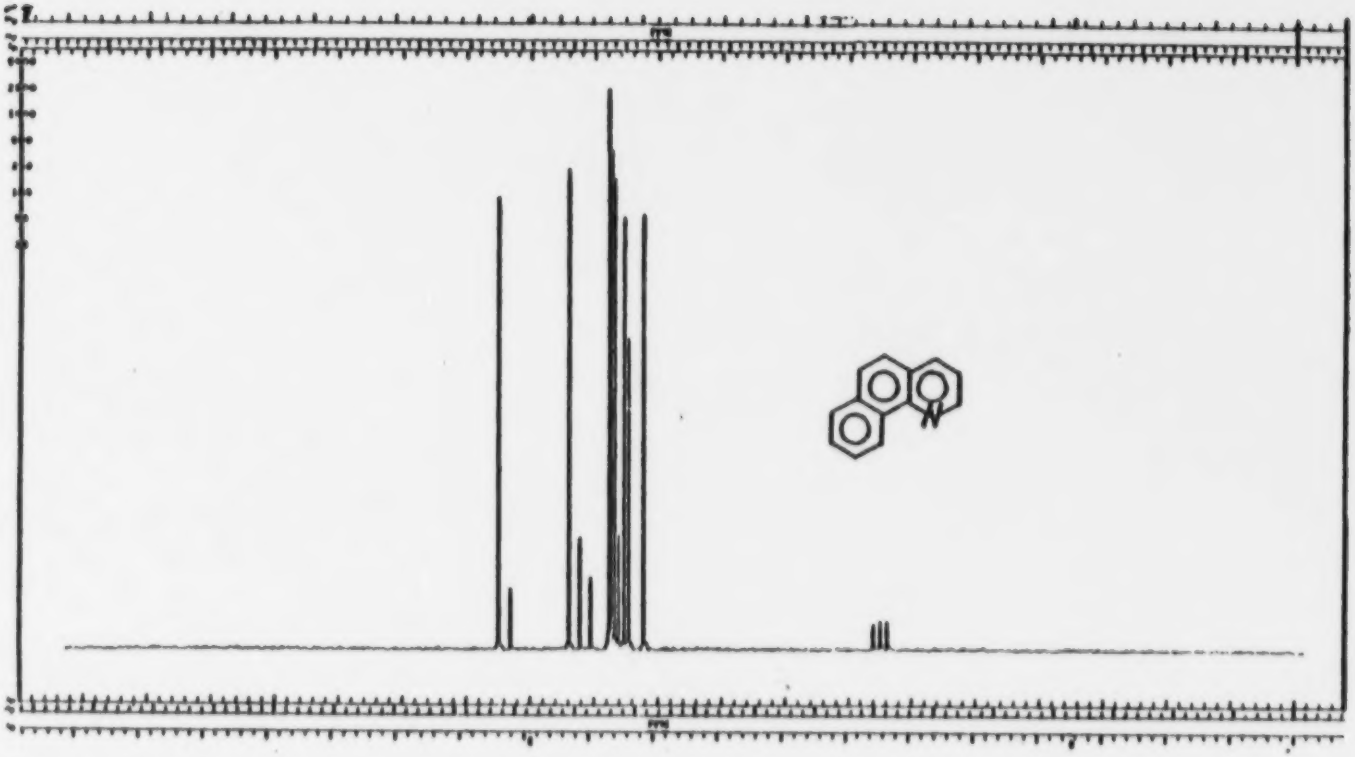


Figure 12b. ^{13}C NMR Spectrum of Benzo[h]quinoline (13) in $CDCl_3$.

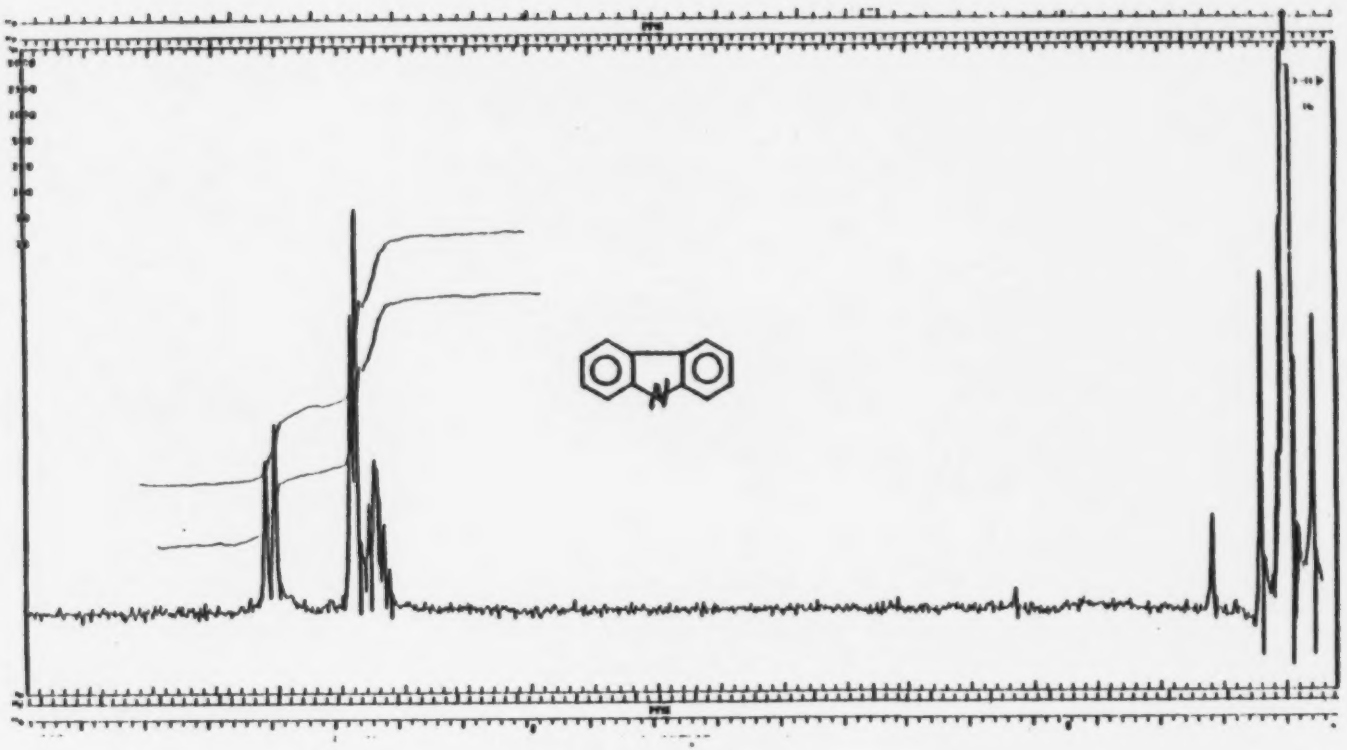


Figure 13. ^{1}H NMR Spectrum of Carbazole (14) at 100 MHz in $CDCl_3$.

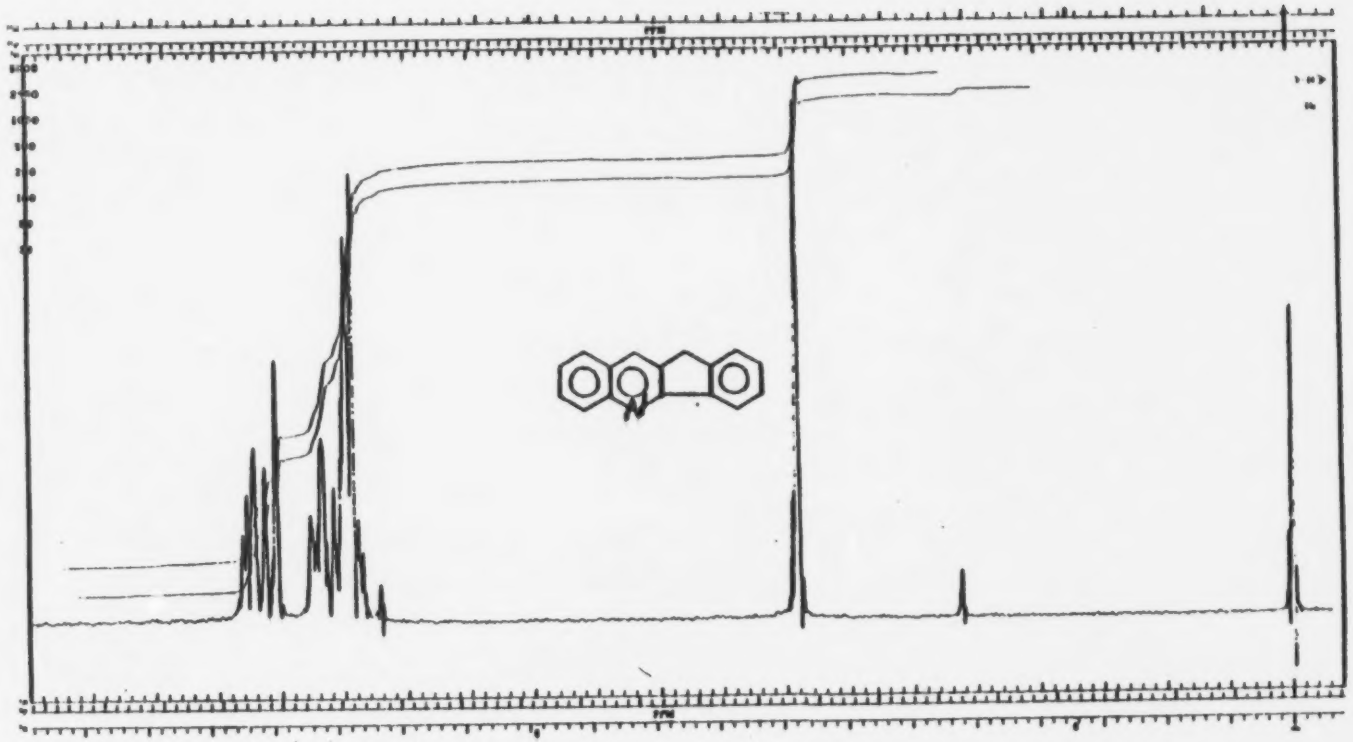


Figure 14. ^{1}H NMR Spectrum of 11H-Indeno[1,2-b]quinoline (15) at 100 MHz in $CDCl_3$.

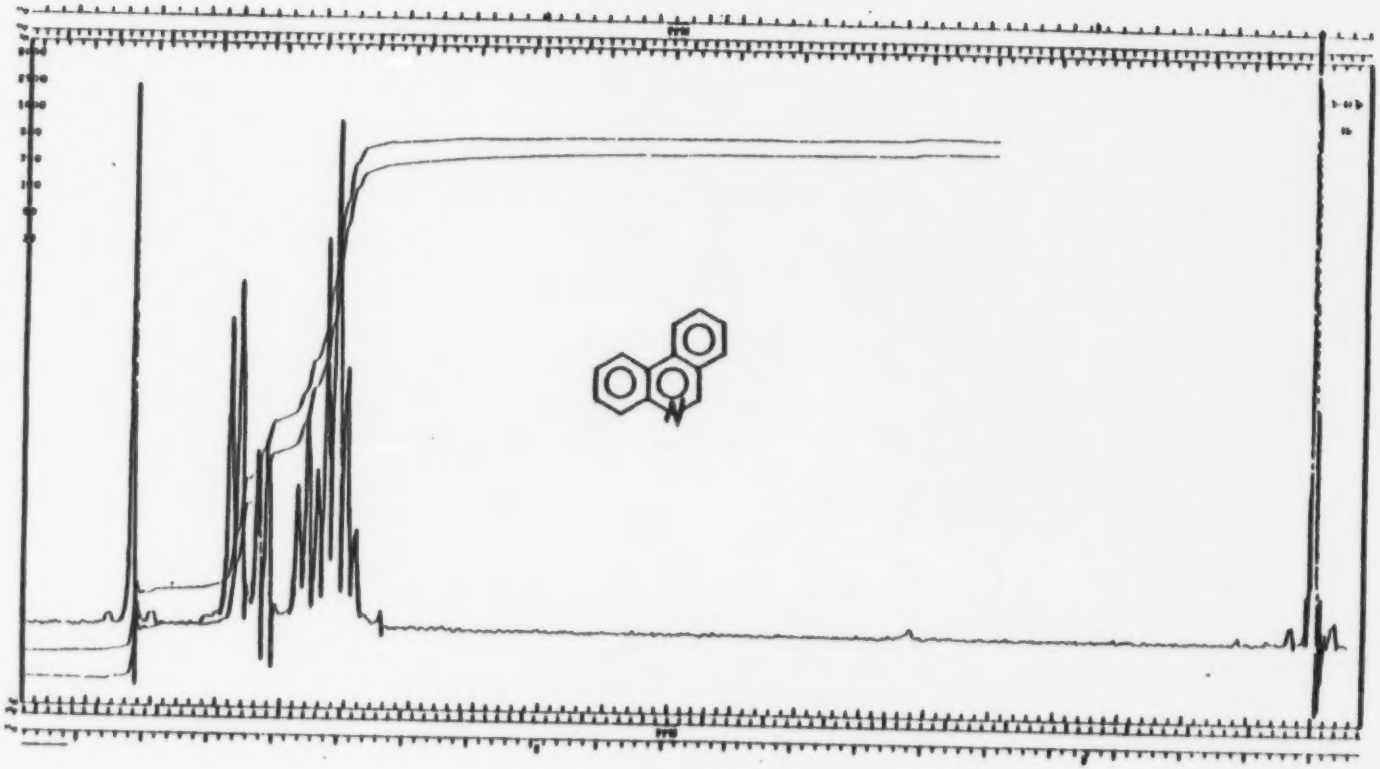


Figure 15a. ^{1}H NMR Spectrum of Phenanthridine (16) at 100 MHz in $CDCl_3$.

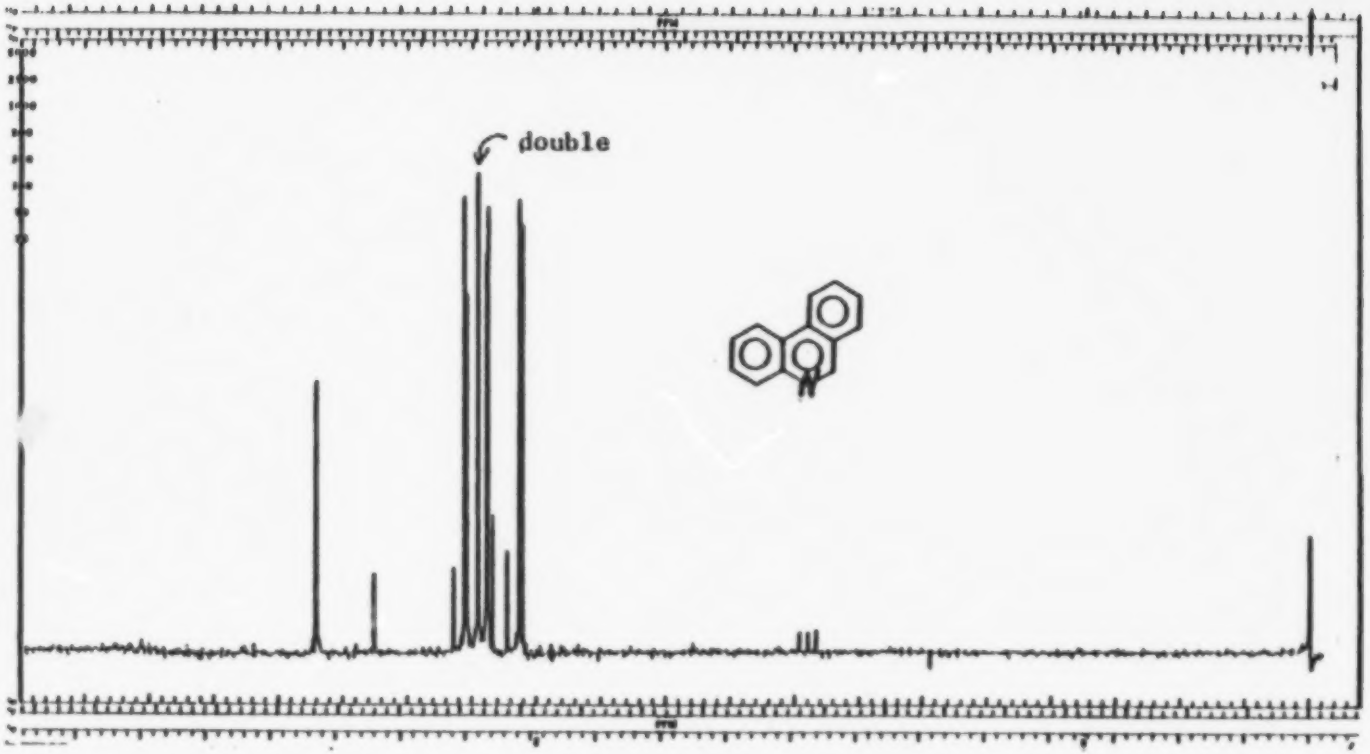


Figure 15b. ^{13}C NMR Spectrum of Phenanthridine (16) in $CDCl_3$.

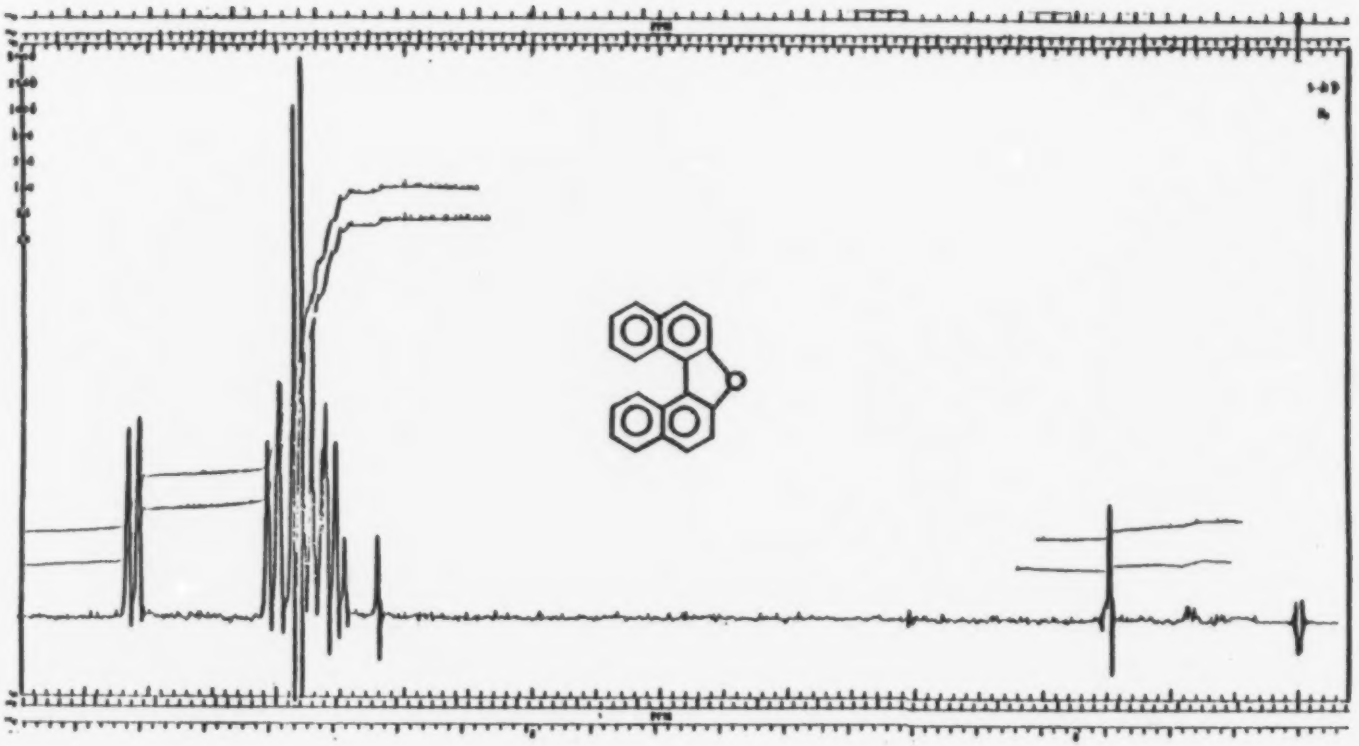


Figure 16. ^{1}H NMR Spectrum of Dinaphtho[2,1-b:1',2'-d]furan (17) at 100 MHz in $CDCl_3$.

Figure 17. ^{1}H NMR Spectrum of peri-Xanthenoxanthene (18) at 100 MHz in $CDCl_3$.

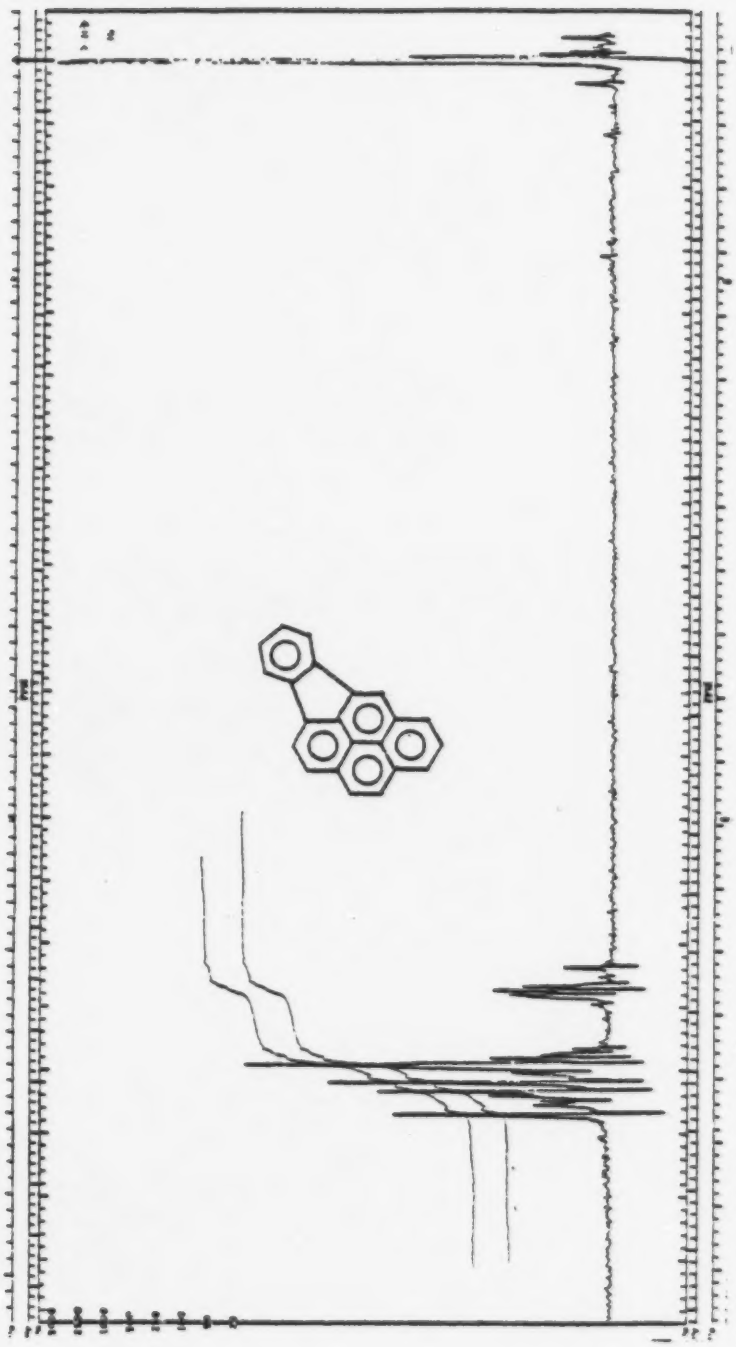


Figure 18a. ^{1}H NMR Spectrum of Indeno[1,2,3-cd]pyrene (51) at 100 MHz in $CDCl_3$.

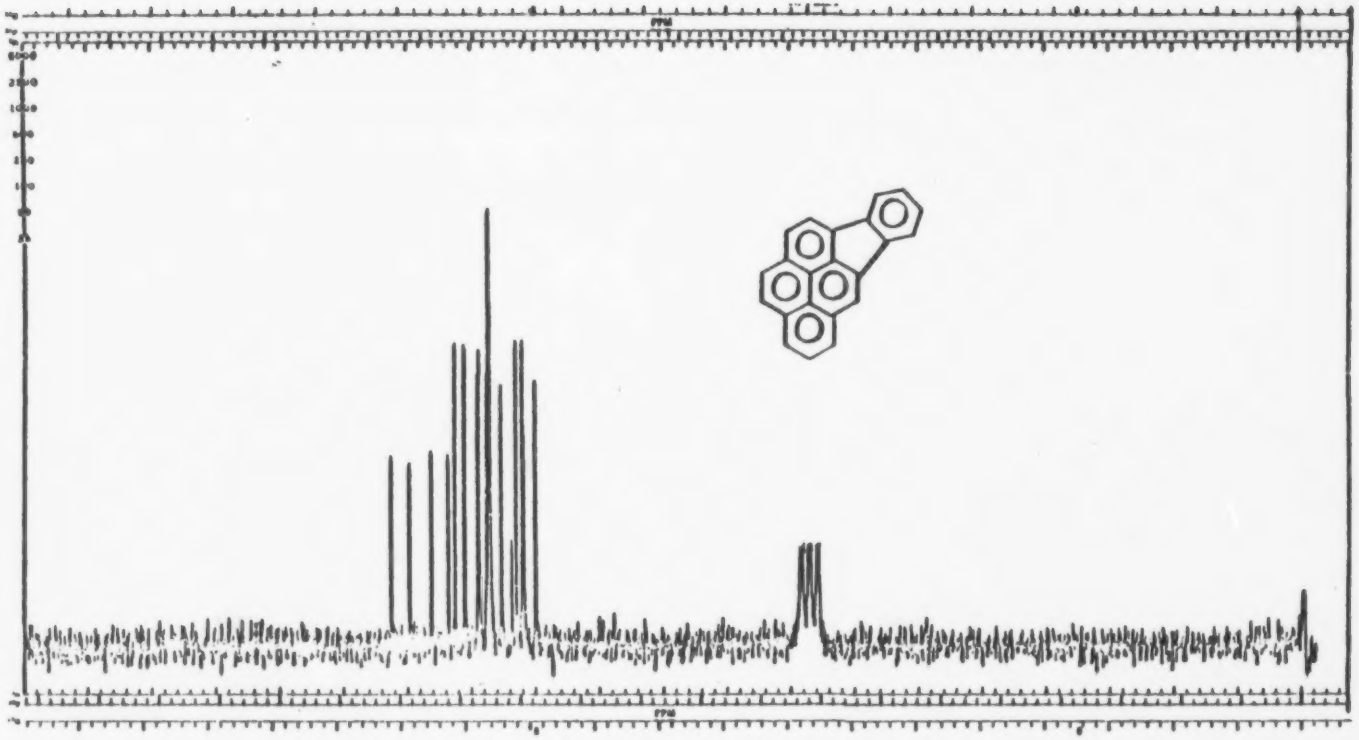


Figure 18b. ^{13}C NMR Spectrum of Indeno[1,2,3-cd]pyrene (51) in $CDCl_3$.

SECTION 6

RESULTS AND DISCUSSION

The objective of this project was to synthesize and purify PNA compounds including hydrocarbons, nitrogen heterocyclics and oxygen heterocyclics of interest to the Chemistry and Physics Laboratory, NERC, Research Triangle Park.

In Section 4 and 5, we present the synthesis routes and the purification techniques used in obtaining pure samples of these compounds. Information about compound names and their structures as well as the melting points and quantities supplied to the EPA is found in Table II and other parts of SECTION 4. To verify the structure and the purity of these compounds, infrared, mass, ^{1}H NMR and in some cases ^{13}C NMR spectra were obtained. The NMR data are reproduced in Figures 3-18b on pp. 38-58. In the case of coronene, its insolubility prevented obtaining a suitable NMR spectrum in a reasonable instrument-time interval and therefore we used mass spectrometry to establish its identity and purity. These data are found in Table 4 on p 26.

In the preparation of the compounds listed in this report, we utilized known routes but also devised new approaches to synthesis and improved the methods of isolation and purification. Some of this work is described in Appendices B and C and a portion has been published as shown on pp.63 and 64.

Because of the carcinogenic nature of several of these compounds, we were forced to develop techniques which improved their safe handling and reduced the chance for laboratory accidents and spills. Since there is considerable current interest in improving laboratory safety, we decided to review our procedures and offer a summary found in Appendix A.

Several theses resulted from this work and the titles are listed on p.63. We are currently attempting to publish as much as practical and the titles of manuscripts under preparation appear on pp.64 and 65.

A portion of our current effort will be reported at a symposium on polynuclear aromatics in San Francisco on Aug 25, 1980. This symposium is sponsored by the Petroleum Division of the American Chemical Society and it will be chaired by Dr. Eisenbraum.

As noted elsewhere in this report, our group synthesizes and purifies compounds for the Thermodynamics Group, U.S. Department of Energy, Energy Research Center in Bartlesville, Oklahoma. As a consequence, precise thermodynamics properties for several of the compounds prepared in this study will be obtained and these data will be published by the Bartlesville group under the supervision of W.D. Good.

FOOTNOTES AND REFERENCES

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5. Equipment, supplies and some costs were shared with the Thermodynamics Branch, Bartlesville Energy Technology Center, Bartlesville OK, U.S. Department of Energy. This assistance is greatly appreciated.

6. High-pressure liquid chromatography studies, analytical and preparative, were carried out using equipment obtained from Waters Associates, Milford, Mass. A microporasil column was used for analytical work. Preparative separations (LC 500) were done with C-18 and silica columns.

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LIST OF THESES, PUBLICATIONS, MANUSCRIPTS, AND SYMPOSIUM

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Manuscripts Submitted

L.F. Pahler, L.L. Ansell, J.W. Burnham, H. Hall, G.J. Mains, W.D. Good, Zone Refining Organic Compounds - Apparatus and Procedure, submitted to American Laboratory. See Appendix B.

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P. Vuppalapaty, L.L. Ansell, and E.J. Eisenbraun, Formation and Acid-Catalyzed Isomerization of Ketones Derived from γ-Arylbutanoic Acids, submitted to J. Org. Chem.

Manuscripts Being Prepared

D.L. Bymaster, G.W. Keen, and E.J. Eisenbraun, Dissolving Metal Reduction of Pyrene.

P. Vuppalapaty, G.W. Keen, and E.J. Eisenbraun, Selectivity in the Chromic Acid Oxidation at the Benzylic Position.

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P. Vuppalapaty, G.W. Keen and E.J. Eisenbraun, The Direct Conversion of 1-Tetralones to Aromatic Hydrocarbons in the Presence of Fused Alkali.

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APPENDIX A

Procedure for Preparing EPA Samples for Shipment

Sample purification frequently involves adsorption of impurities on acidic or basic alumina or silica gel. To improve this procedure we developed[1] the Soxhlet apparatus shown in Fig. 1. We also made extensive use of sublimation and Fig. 2 shows a current apparatus design.[2]

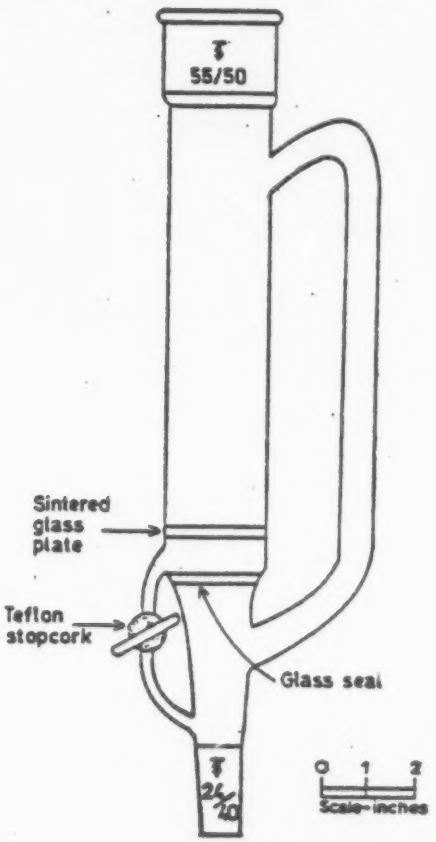

Figure A-1 An Improved Soxhlet Apparatus.

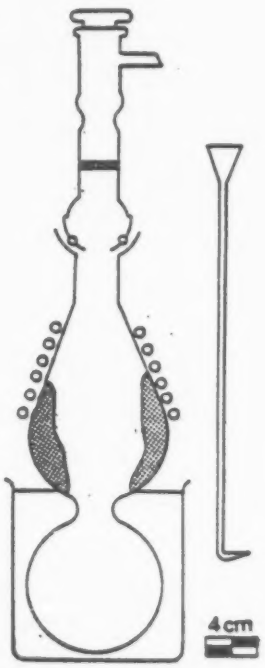

Figure A-2 An Improved Sublimation Apparatus.

In order to efficiently and effectively fill a large number of vials and to make certain that the sample weight is correct, permanent decals are placed on individual vials. One-gram, screw-cap vials are rinsed with

distilled water, the decals (1-100) are attached, and the vials are then fired in an annealing furnace at 560°C to fix the decal. Heating at this temperature burns any carbon inside the vial, ensuring clean vials. The use of numbered vials enables rapid sorting with a minimum of error in weighing and handling. The vials are sorted, loosely capped and placed in stainless steel racks.

Use of Glove Bag in Transferring Samples

Most of the compounds are sensitive to oxygen and/or are toxic. Therefore, a nitrogen-filled glove bag is used in filling the vials. Fig. 3 shows how a glove bag is attached to a N_2 line. We have found the 27" x 17" I^2R glove bag size to be convenient. A list of items which have been found to be useful in filling the vials appears below. This list is in two parts; one is for components required for assembling the glove bag, and the other is for items required inside the glove bag. It is recommended that the glove bag be assembled and all of the components, including the pre-weighed vials contained in their racks, be placed inside the glove bag and the glove bag sealed as shown in the drawing. Argon or nitrogen is used to inflate the glove bag. The glove bag is then deflated with a vacuum pump until the plastic walls tightly pull around the various objects. The intent is to dimish the air supply inside the glove bag and the loosely capped vials. The glove bag is re-inflated and pumped out for at least three filling and two pumping operations. During this operation, the compound remains sealed inside the sublimation flask or storage bottle. Removal of the sample from the sublimation flask can be facilitated

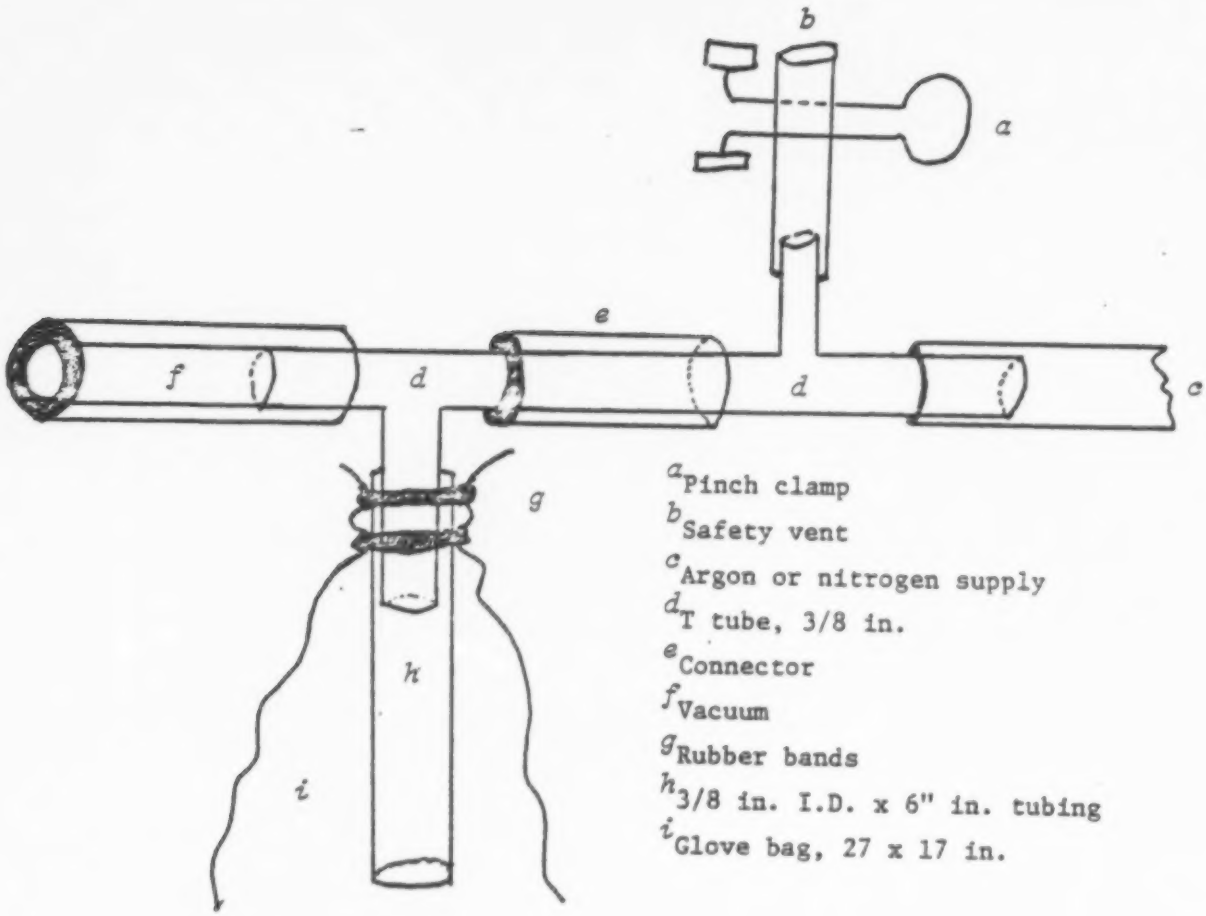

Figure A-3. Nitrogen Supply and Vacuum Source for Glove Bag

through use of the spatula shown in Fig. 2. The sublimed or pumped sample is placed in a small beaker via a funnel or in a petri dish (it will depend upon the packing characteristics of the compound whether a petri dish or a beaker is used) and then transferred to individual vials through use of the solid sample dispenser[3] shown in Fig. 4.

Working over a Pyrex pie plate or cake pan is advantageous because any spilled material is retained and can be collected later. Great care should be taken in transferring compound from storage container (petri dish, beaker, or bottle) so as to reduce contamination of the exterior of the vials.

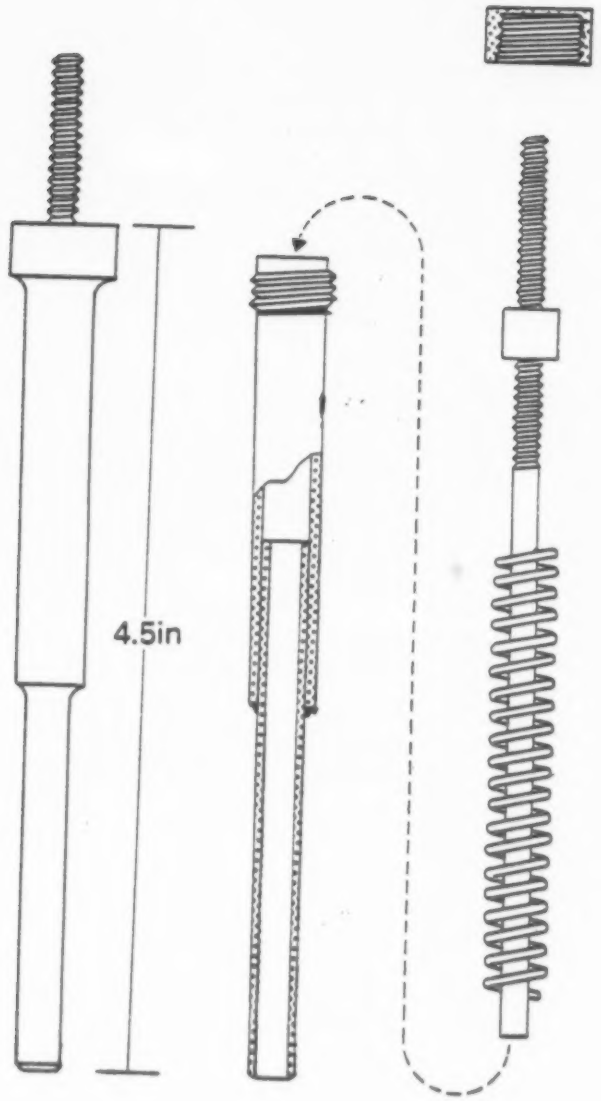

Figure A-4. Solid Sample Dispenser.

After all of the vials are filled and capped, the inert gas supply c is clamped off and disconnected from the glove bag.

The glove bag is usually mounted on a 2' x 3' board and thus the entire assembly can be conveniently transported to the hood, the glove bag is cautiously deflated and opened. All of the contents of the glove bag are then removed and sorted. If toxic material is being handled, the tools may

be placed in a Soxhlet apparatus of Fig. 1 or in the apparatus[4] shown in Fig. 5 for thorough extraction or they may be rinsed with dichloromethane and then ignited in the annealing furnace to burn carbon residue. The glassware is rinsed with dichloromethane and then placed in a Pyrex cake pan for ignition.

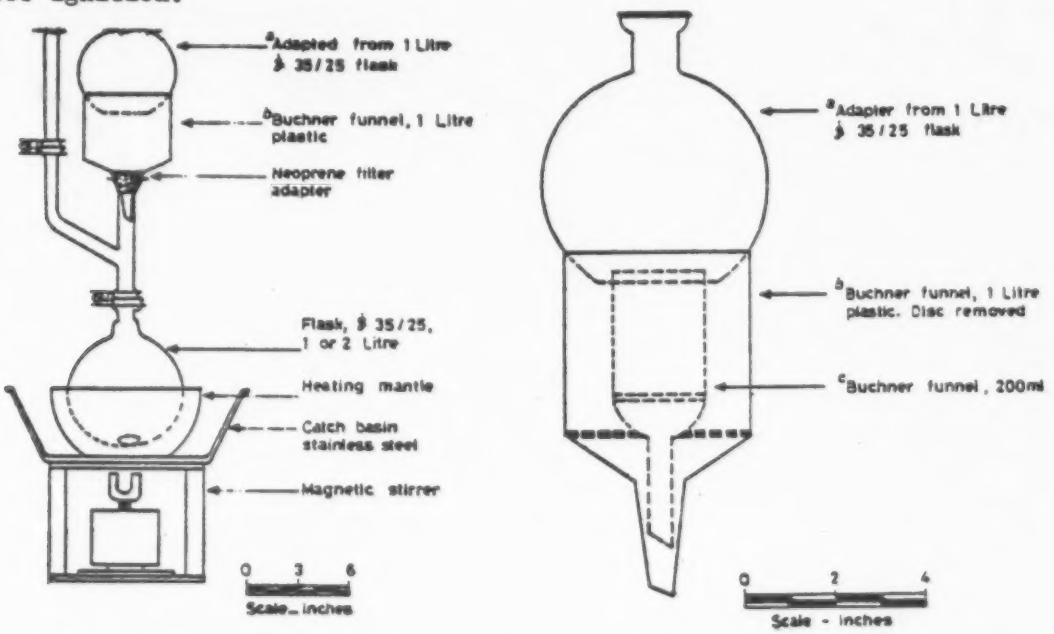
[a]Adapted from 1 Litre ⅄ 35/25 flask
[b]Buchner funnel, 1 Litre plastic
Neoprene filter adapter
Flask, ⅄ 35/25, 1 or 2 Litre
Heating mantle
Catch basin stainless steel
Magnetic stirrer
0 3 6
Scale - inches
[a]Adapter from 1 Litre ⅄ 35/25 flask
[b]Buchner funnel, 1 Litre plastic. Disc removed
[c]Buchner funnel, 200ml
0 2 4
Scale - inches

Figure A-5. An Apparatus for Cleaning Sintered-Disc Buchner Funnels and Other Laboratory Items.

The anhydrous conditions inside the glove bag usually causes generation of static electricity. This should be considered in handling toxic compounds.

Glove Bag Components

1. Glove bag, I^2R, 27" x 17"
2. Dowel, 0.5" x 2'
3. Plastic T tubes, 3/8" as shown in Figure 1
4. Pinch clamp

Glove Bag Contents

1. Compound, sealed in sublimation vessel or bottle.
2. Steel vial racks, numbered 0-100
3. Vials, decaled and weighed, caps loosened

5. Ball and socket clamp No. 35 (to fasten dowel)

6. Tube, vacuum, rubber, item *h* of Figure 1

7. Plywood base, 2' x 3'

4. Solid sample dispenser, stainless steel, for use with Petri dish. This apparatus is adjustable and permits variable sample size.

5. Spatula, micro and Spoonula

6. Scraper to remove sample from sublimation vessel (see reprint)

7. Forceps

8. Pyrex cake pan, 9" x 15"

9. Petri dish or beaker for sample

Cleanup and Labeling

The filled vials are gently spilled into a Pyrex cake pan for cleaning. The emptied stainless steel vial holders are then thoroughly cleaned with solvent to remove any toxic compound. The individual vials are wiped with Kleenex tissue moistened with dichloromethane (to reduce the amount of contaminated paper from this operation, Kleenex can be cut into small pieces). This paper is added to the large-mouth collection bottle along with any solvent used in cleaning the tools and vials. The collection bottle and glove bag are placed in the carcinogen storage container for disposal. Precaution: at this point, as in all the operations in which a toxic compound is involved, gloves, apron, protective sleeves, and surgical face mask are worn. After the vials have been wiped with dichloromethane, they are weighed, and the weight is recorded by vial number. Once the sample weight has been determined, the inventory is prepared and the vials are labelled and taped. Considerable care must be taken in taping the vials since the necks are easily twisted off. A novice should intentially shear several empty vials in order to gain an appreciation

of the force required to twist off a vial neck during the cap-tightening process.

The final step is to prepare the vials for shipment, which consists of rolling three or four vials in a folded double Kleenex tissue and securing with rubber bands.

Equipment Needed for Cleanup

1. Dichloromethane and/or acetone wash bottle
2. Cake pan, Pyrex, 9" x 15"
3. Funnel, 6-8" for rinsing into collection bottle
4. Large-mouth collection bottle
5. Kleenex cut to 2" squares
6. Petri dish for dichloromethane

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APPENDIX B

Zone Refining Organic Compounds - Apparatus and Procedure

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Zone refining as a physical method of separation, [1,2] especially for removal of minor impurities from solid semiconductors and metals [3] and as an ultrapurification technique[4], is well established. In as much as depletion (or enrichment) of a minor component in the solid phase relative to the liquid phase is a common phenomenon, the application of multiple-pass zone refining of solids should have found broad application in organic chemistry research laboratories along with other separation processes such as fractional distillation, fractional crystallization, preparative gas chromatography, and high-pressure liquid chromatography, as well as preparative thin-layer chromatography. While Pfann[3] lists over two hundred organic chemicals purified by zone melting, this is miniscule compared to the potential number to which the technique could be applied. Why has zone refining not found wider acceptance in organic laboratories? Since competitive techniques often require more expensive equipment, economics is not the answer. The barrier to usage must reside in unfamiliarity and/or an unwillingness to develop the necessary skills.

We have had good and bad experiences with zone refining both in equipment

and the chemical being purified. Most of our difficulties could be traced to lack of experience and ineffective equipment. The remainder of this paper will be directed to describing these difficulties and our attempts to improve the zone refining apparatus and procedure to an effective and routine purification method.

These points are summarized as follows and are individually treated later in the paper:

1. Purity, stability, and size requirements of the sample.
2. Zone-refining apparatus design - horizontal vs vertical tube mounting.
3. Modification of zone-refining apparatus.
4. Pretreatment of the annealed sample tube.

Initial treatment of the sample through distillation, sublimation,[5] modified Soxhlet extraction[6] through alumina, silica or picric acid[7] or crystallization is generally advisable. We have applied some or all of these techniques, as appropriate, to individual compounds and found that a minimum starting purity of 99% generally insures the production of an ultrapure sample after zone refining.

In addition to the initial purity requirement, it is essential that the molecule be stable to the zone refining temperature conditions. Since hydrocarbons lack functional groups, they are ideal for zone refining. However, they are frequently susceptible to air oxidation (hydroperoxide formation) and thus it is essential that an inert atmosphere be used during tube loading, zone refining, and removing the sample from the zone-refining sample tube. Further, practical usage of zone refining is limited to solids having a melting point exceeding the temperature of the environment of the apparatus or cooling must be provided.

The design of the zone-refining apparatus, whether the sample tube is

moved in the vertical or horizontal manner, can be an important factor. Our first zone-refining apparatus[8] was of the horizontal-tube type in which the tube rotated as it advanced past the heaters. The motion of the tube was regulated through use of a complicated set of plastic gears which were very susceptible to dust and easily became erratic in performance. Consequently, the tube movement became irregular and stalling was frequently observed. All attempts to use this apparatus resulted in tube rupture or other accidents and consequently we were forced to abandon its use. We next acquired a zone-refining apparatus with a vertically suspended tube.[9] This is a considerable design improvement over that using a horizontal tube.

We found it necessary to make the following modifications to the vertical-tube instrument as discussed below and shown in Fig. I. In order to effectively utilize the nine heaters provided with the instrument, it became necessary to include individual secondary heater controls. To this end, 100 ohm, 50 watt, wire-wound variable resistors were installed on the outside of the cabinet (part e, Fig I) and connected in series with each heater (part c, Fig I). During operation, the temperature is adjusted using the primary heater control (part of f, Fig I) which effects all nine heaters. The primary heater control has a selection switch which also supplies heat only to alternate heaters. Final temperature regulation is accomplished using the individual secondary heater controls installed as a modification. This fine tuning ensures narrow liquid zones and enables use of all nine heaters, and thus provides maximum purification per pass.

Fig I also shows the air vent g and the exhaust fan a which were installed as modifications to improve heat dissipation. It should be noted

that zone refining demands careful control of both the heating and cooling.

Fig II shows the copper adapters developed in order to use sample tubes of different diameters than those initially used with the instrument. This permitted reducing the ingot size from about 200g to any smaller amount. We generally use tubing containing ingots of 100g, 50g, and 30g. This involves medium wall sample tubes having 25, 18, and 12 mm diameter, respectively. Considerable care must be exercised in the selection of smaller tubing. Wall thickness provides rupture protection but increases the thermal mass of the container relative to the sample, reducing control of the molten zone length.

In earlier stages of our work, we experienced frequent rupture of the sample tube. We considered that wetting of the interior walls of the zone-refining tube by sample was a primary cause. Treatment of the annealed tube with SC 87[10] was used to reduce interaction of sample with the interior wall. We found SC 87 to be effective in reducing tube breakage. However, some poly-nuclear compounds still rupture the glass or adhere to it so tightly that the refined compound can not be removed except by shattering the sample tube. In most cases, as will be described later, the sample can be removed by boring[11] into the chemical contained in a severed section of tubing and shaking out the loosened material.

The glassware shown in Fig III is used in the tube filling process. Exclusion of oxygen from the sample contained in e is accomplished by repeated flushing of the assembled components a, e, and h with argon. The system is then evacuated to 0.1 mm Hg, the sample is melted into tube h by heating with heat tape d and/or a Heat Gun (110 V, 12 Amp, 500°C) and heating jacket j. Once the sample has been introduced to tube h and degassed, it is allowed to cool to room temperature[12]. Stopcock a of Fig III is then closed, disconnected

from the vacuum-argon line, and the apparatus (parts a, e, and h of Fig III) is then transported to the glassblower[13] for sealing and adding a hook.

Table I summarizes data gained from zone refining 8 hydrocarbons. In addition, we have carefully zone refined acridine, benz[*a*]anthracene, 5,6-benzoquinoline, carbazole, 2,6-di-*tert*-butylnaphthalene, 1,2,3,6,7,8-hexahydro-pyrene, phenanthrene, 4,5,9,10-tetrahydropyrene. Of these 5,6-benzoquinoline and carbazole survived 36 and 10 cycles respectively before the tube ruptured. We await data on the remaining compounds.

The filled zone-refining sample tube is then mounted in the apparatus as shown in Fig I. Molten zones are established through use of the primary and secondary temperature controls parts f and e of Fig I, respectively. The apparatus is allowed to cycle through 75 or more passes.

As mentioned above, we have experienced tube rupture and have not observed a consistent pattern for this failure. In each case, we believe the tube developed pressure at the top as a result of sublimation and ingot creeping. If significant creeping of sample to the top of the tube is observed, rupture generally follows. We have melted the upper portion of the ingot with a Heat Gun in an attempt to avoid creeping. However, this alters purification of that portion and the adjacent portion in subsequent cycles.

In those cases in which exposure of compounds to oxygen is prohibited, we use the apparatus shown in Fig IV to provide an inert gas shield during fracturing of the sample tube with the molten tip of a glass rod. This is accomplished by scoring the tube[15] in the apparatus of Fig IV and then maneuvering the tube so that a given scratch is situated below a side port. A heated glass rod is then inserted to touch the etched tube to crack it

at that location. The apparatus of Fig IV is then transferred to a glove box for further manipulation and removal of sample for calorimetry and other analyses[16].

In conclusion, we feel that most of the problems associated with zone refining organic solids have been overcome or minimized and that application of the above techniques should enable wider usage in purification of organic compounds.

Acknowledgements. We thank the Bartlesville Energy Technology Center (contract EW-78-A-19-0) and the environmental Protection Agency (grant R 80 541-03-0) for partial support. The contents do not necessarily reflect the views and policies of these agencies, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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8. Materials Research Corp., Orangeburg, New York 10962 - Multizone I.
9. Princeton Organics, Route 206, Princeton, New Jersey 08540 - Ultrazone Refiner.
10. We thank H. Planchard, Laramie Energy Technology Center, Laramie, Wy. for this suggestion. SC87 is available from General Electric, Silicone Prod., Waterford, New York 12188.
11. A flat wood boring bit, 1/4", fitted with a handle is used.
12. The sample should be solidified progressively from the bottom, otherwise the sample rises to the upper portion of the tube and through the opening.
13. We thank Mr. M. W. Adkins for assistance in sealing the tubes.
14. H. L. Finke, J. F. Messerly, S. H. Lee, A. G. Osborn, and D. R. Douslin, J. Chem. Thermodynamics 937 (1977).
15. We customarily score the tube in seven evenly divided lengths.
16. Samples are taken for GC and HPLC analysis.

Table I. Compounds Purified Through Zone Refining

Compound	Emperical Formula	°C Melting Point	% Purity Achieved
1,8-Dimethylnaphthalene	$C_{12}H_{12}$	63.178	99.9955[a]
2,6-Dimethylnaphthalene	$C_{12}H_{12}$	110.167	99.958[a]
2,7-Dimethylnaphthalene	$C_{12}H_{12}$	95.663	99.95[a]
Fluorene	$C_{13}H_{10}$	114.793	99.992[a]
1,2-Dinaphthylmethane	$C_{21}H_{16}$	96.396	99.90[a]
Pyrene	$C_{16}H_{10}$		99.981±0.004[b]
Fluoranthene	$C_{16}H_{10}$		99.991±0.005[b]
8,9-Trimethylenephenanthrene	$C_{12}H_{14}$		99.990±0.004[b]

[a] Calorimetric purity (reference 14).

[b] CO_2 Detn. (mean + s.d.m.)

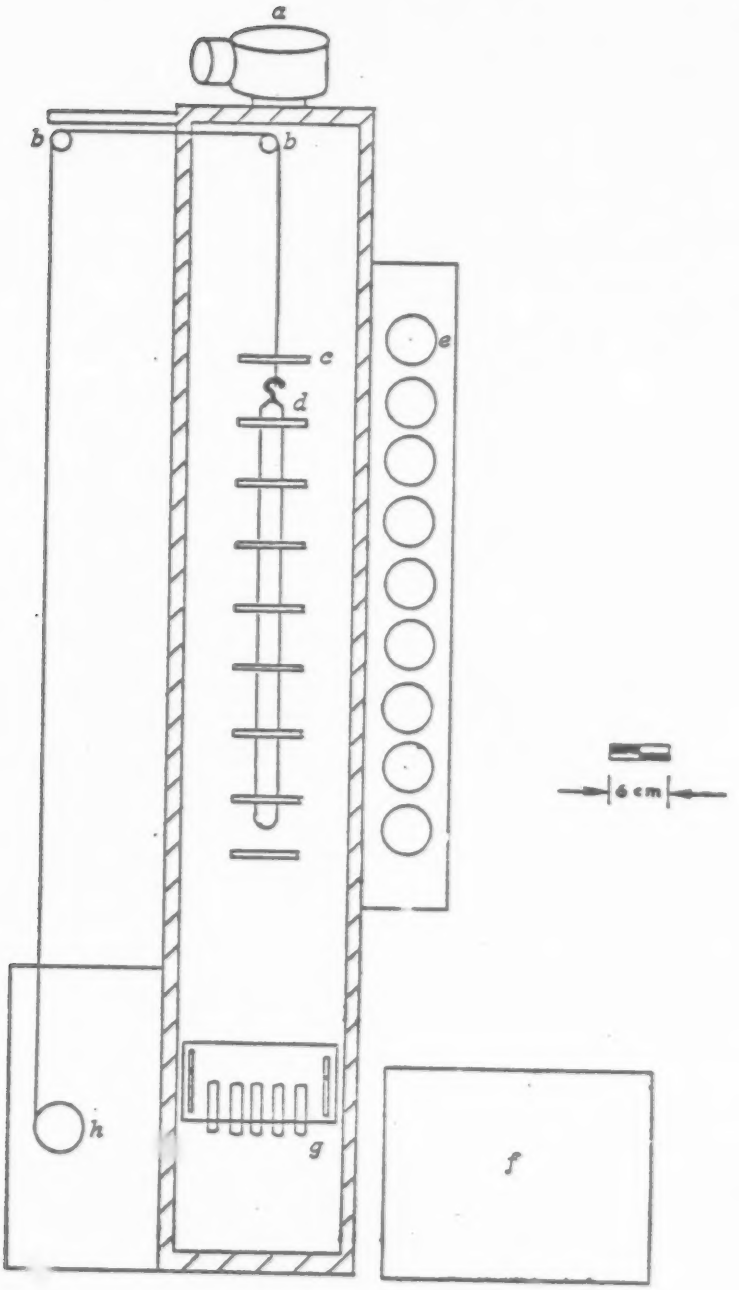

Figure B-1. Modified Zone-Refining Apparatus.

Legend for Figure I

[a] Variable speed exhaust fan, a modification

[b] Suspension pulley for zone-refining tube cable

[c] Heater, 50 watts, 100 ohms, 9 each

[d] Zone-refining tube

[e] Wire-wound, 100-ohm, 50-watt, variable resistors installed in series with each heater. These secondary temperature controls were installed as a modification

[f] Electronic power supply, cycle counter, and primary temperature control

[g] Air vent, a modification

[h] Zone-refining tube lowering and rewind mechanism

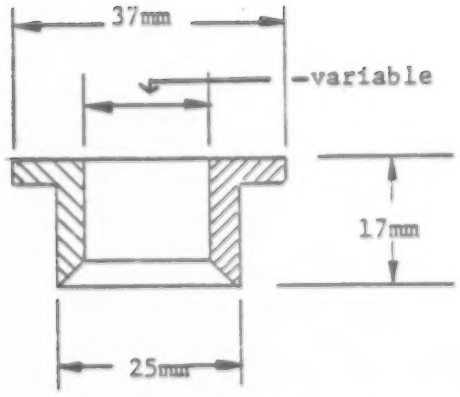

Figure B-2. Zone-Refining Tube Adapter

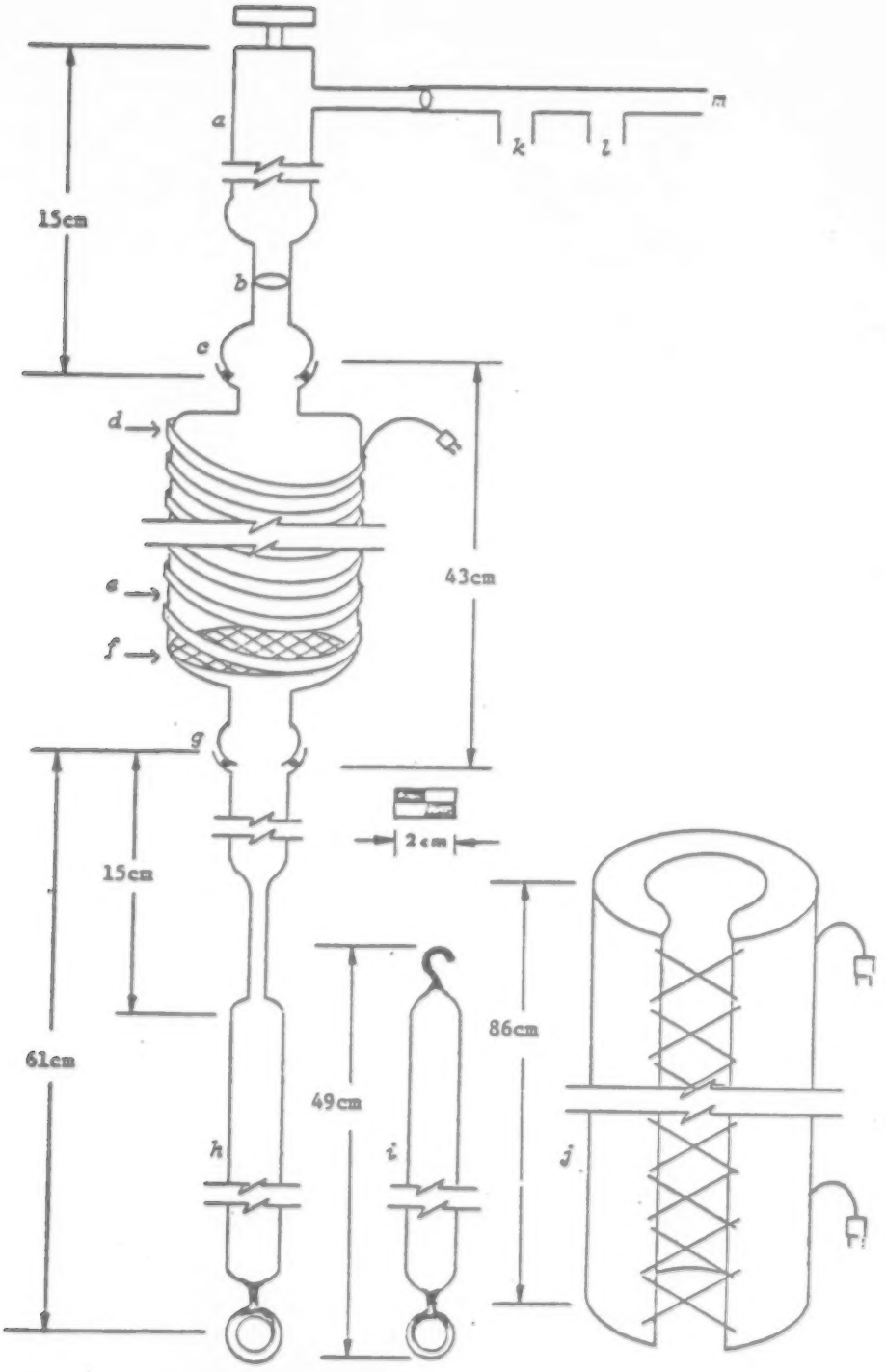

Figure B-3. Apparatus for Filling Zone-Refining Tubes

Legend for Figure III

[a] High vacuum stopcock, 4mm, Corning 7548 fitted with tubing leading to a mercury filled manometer, vacuum pump and argon source

[b] Coarse glass frit

[c] O-ring ȣ, 51/35. These are available from Chemvac Associates, 852 Malibu Drive, Columbia, South Carolina 29209. Ace Glass Co., P. O. Box 688, Vineland, New Jersey 08360 ₮ 7648, O-Ring seal may also be used.

[d] Heating tape

[e] Glass sample container

[f] Glass grid to support sample

[g] A ȣ 35/20 is used - cf. footnote *c*

[h] Annealed glass sample tube treated with SC 87

[i] Filled sample tube

[j] Heating jacket obtained from Glas-Col Apparatus Co., Terre-Haute, Inc.

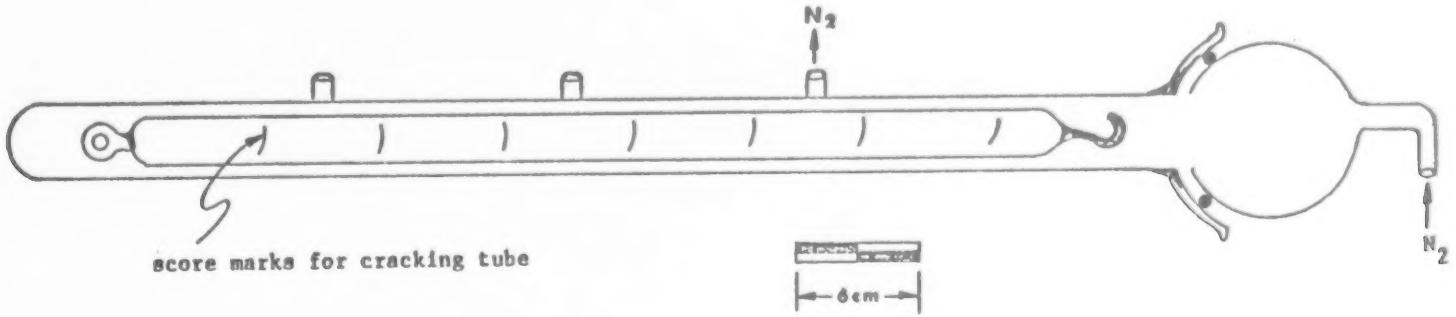

Figure B-4. Apparatus for Opening Zone-Refining Tubes under an Inert Atmosphere

APPENDIX C

A High-Temperature Sand-Bath Heater

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We recently described a sublimation apparatus using water (0-60°C), oil (50-220°), Wood's metal (80-300°C) or a fused mixture of KNO_2:$NaNO_3$ (10:7) (145-350°) as the heating bath medium[1]. None of these is adequate for high temperature work (350-500°C). The latter is the upper working limit for glass apparatus under vacuum.

There are fluidized-bed heaters[2] for high temperature work but these are expensive and we are not aware of other designs suitable for a reaction range of 1 mL to 1 L. Our design encompasses the entire size range but it may be convenient to build a smaller heater for some purposes. Because of possible flask rupture, we were unwilling to use reactive chemicals as the heater filler and settled on dry sand[3] as the most suitable medium.

The heater in Fig. 1 is constructed by encircling the stainless steel cylinder b with 3 nigh temperature band heaters a.[4] The post terminals provided with the heaters were found to be easily damaged and consequently we developed the sturdy copper conductor d and its ceramic support e as an improved electrical connection. Parts d and e are anchored securely to the aluminum frame c. To withstand the high temperature, 12 gauge, single strand copper wire leads were used. A ground to the aluminum frame was also installed. The multiple size lid f provides an adequate cover for reaction flasks.

Thermal insulation is provided by a layer of Pyrex wool fiber covered wtih several layers of glass tape. The thermal insulation provides some

electrical insulation. However, if electrical insulation is critical it may be achieved by surrounding the heater with a ceramic cylinder.

At 110 volts the three heaters will require about 2 h to provide approximately 500°C at the center of the bath filled with sand. If equal potential is applied to the three heaters, the upper portion of the sand bath will become hottest (10-20°C) but since the heaters are independently wired, the vertical temperature gradient can be controlled.

The glass apparatus of Fig. 2. is an adaptation of a previously described sublimation apparatus.[1] Use of Clear-Seal joint[5] b is advantageous since this allows the receiver c to be changed and thus makes fractional sublimation possible. Another advantage to using a Clear-Seal joint is that lubrication is not needed to retain a vacuum (0.1 mm). The course frit at e of Fig. 2. was added to prevent passage of sublimate and is useful in preventing return of particulate matter and stopcock grease to flask c when the vacuum is released through the 3-way stopcock f. Using the 3-way stopcock f permits introduction of an inert atmosphere before and after sublimation or evacuation. Surprisingly, the frit e did not clog with sublimate when used with perylene, coronene, and coronene-1,2-anhydride, although sublimate was carried to that point.

Acknowledgement. We thank the Environmental Protection Agency under grant R805419-010 and the Bartlesville Energy Technology Center under Department of Energy contract DE-AT19-78BC31001 for support.

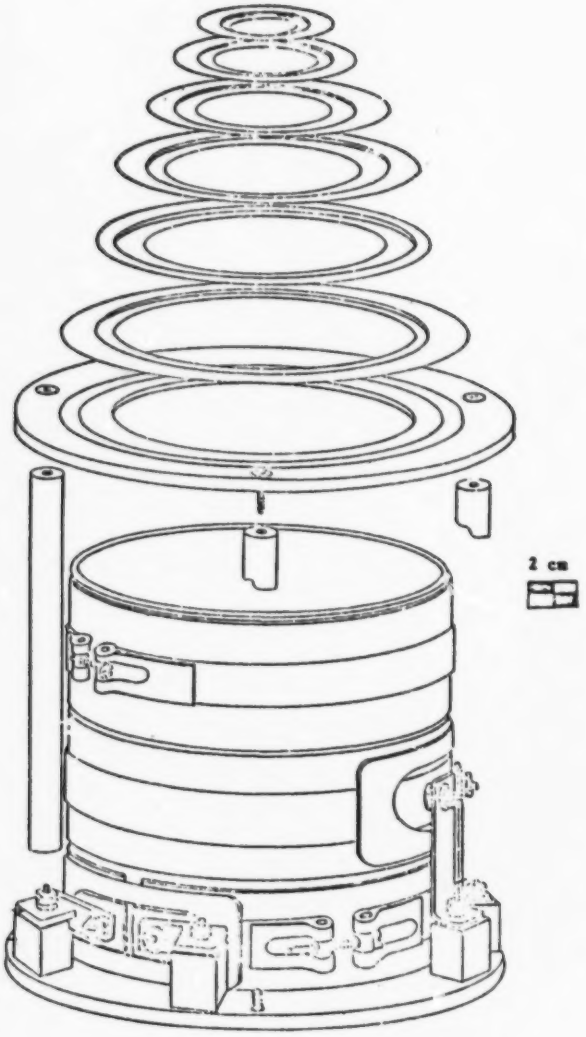

Figure C-1. Flask Heater

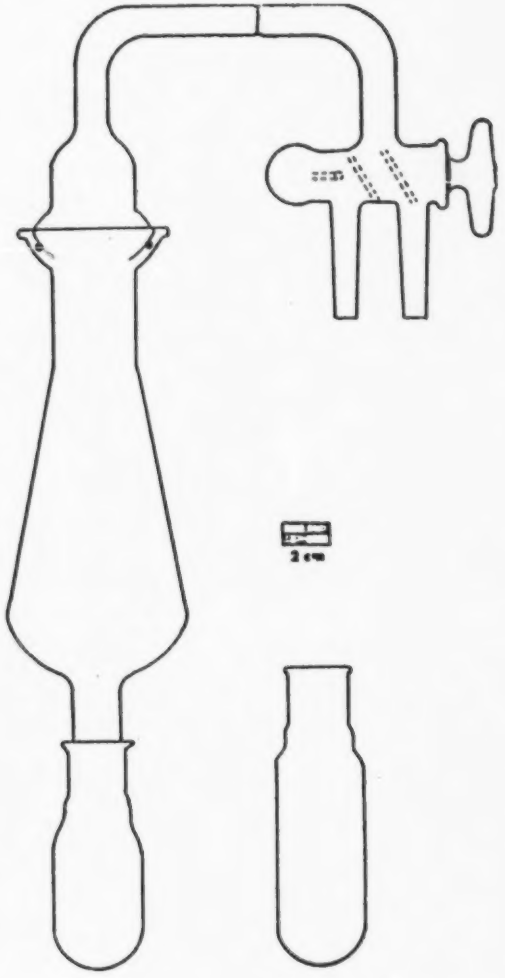

Figure C-2. Glass Reactor Assembly

Legend for Fig 1

[a]Band Heaters, high temperature, Code No. 30845A. See also ref 4

[b]Stainless steel liner, 1.6 mm x 15 cm diameter x 15 cm high

[c]Aluminum support

[d]Copper conductors

[e]Ceramic blocks

[f]Reactor lid, multiple size, from commercial steam bath

Legend for Fig 2

[a]Flask built as shown or constructed as a sphere

[b]Joint, T 24/25. See also ref. 5

[c]Sublimation flask. See also ref 1

[d]Joint, ball and socket, O-ring, 50/30, Chemvac Associates, 825 Malibu Drive, Columbia S.C., USA or G.M. Associates, Inc., 1912 Everett St., Alameda, CA., USA

[e]Coarse frit

[f]Stopcock, high-vacuum, 3-way

References

(1) Eisenbraun, E.J., Moyer, C.J., and Vuppalapaty, P. Chem. Ind., 229 (1978)

(2) Techne Inc., 3700 Brunswick Pike, Princeton, N.J. 08540, USA

(3) Alumina is used in commercial fluidized-bed baths [2]

(4) High temperature band heater, 5 cm wide x 15 cm diameter, Watlow Code No. 30845A, 110 Volt, 425 Watt, Watlow 12001 Lackland Rd., St. Louis, MO. 63141, USA

(5) Joint, T 24/25, Clear Seal, Wheaton Scientific, 1000 N. Tenth St., Millville, N.J. 08332, USA

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